THE SILICATES

IN CHEMISTRY AND COMMERCE

INCLUDING THE EXPOSITION OF A HEXITE AND PENTITE THEORY AND OF A STEREO-CHEMICAL THEORY OF GENERAL APPLICATION

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LONDON

CONSTABLE & COMPANY LTD.

10 ORANGE STREET, LEICESTER SQUARE, W.C.

1913

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PREFACE

IN the year 1903, the Faculty of Philosophy in the University of Göttingen proposed the following thesis in connection with the Benek Bequest :

A critical examination, based on experimental evidence, is to be made of such chemical compounds as cannot be satisfactorily explained by the usual means. This examination should also take into special consideration the extent to which the introduction of molecular additions is of importance in the formation of such compounds, and whether it is possible to devise a complete systematic arrangement of such compounds.

Under the motto :

"Πάντα (Θεὸς) μέτρῳ καὶ ἀριθμῷ καὶ σταθμῷ διέταξε"

the authors submitted a thesis which forms part of the present volume, viz. pp. 1 to 102 and the *Appendix*. The solution of the problem was admittedly incomplete, inasmuch as only a single branch of the subject —the silicates—was taken into consideration. For this reason the Faculty did not grant the first prize to this thesis, but readily granted the second prize " in recognition of fruitful labours leading to a single theory covering a very important group of complex compounds."

In this way an established theory—the Hexite-Pentite Theory—was devised for one highly important group of complex compounds—the silicates.

With this theory in mind, it was only natural to apply it to a series of silicates of technical and commercial value, such as the ultramarines, Portland, slag, dental and other siliceous cements, glass, glazes, porcelain, etc., in order, if possible, to elucidate their constitution. This has been effected since the original thesis was first written, and the results are published in the following pages.

Commencing with the assumption that Nature has formed all substances in accordance with monistic laws, the Hexite-Pentite Theory has also been applied to the study of the structure of other complexes as well as to that of solutions of the simpler acids, etc., and it has also been employed, in connection with the constitution of organic compounds, to form a bridge between organic and inorganic chemistry.

In order to take into consideration the positions which atoms occupy in space (a factor which is omitted from most theories of chemical structure) the Hexite-Pentite Theory has also been developed, in combination with the modern theory of the structure of crystals, into a *stereo-chemical theory*.

The German edition of this work was published late in 1911, but for some unexplained reason almost every reviewer of that edition failed to appreciate the advantages which may be derived from this theory, and with a few exceptions they have overlooked the fact that the Hexite-Pentite Theory—as distinct from older ones—is concerned especially with inorganic chemistry, and that it has the following characteristics :

The Hexite-Pentite Theory is a general and unitary theory ; it is based on a single truth—i.e. on a natural law found by inductive reasoning ; it leads *par excellence* to prognoses, and therefore permits of deductive reasoning—the combination being a clear sign of a true theory—and it is, in addition, based on the methods of the most famous classical chemists. Moreover, it comprehends the best of the existing theories or explains their deficiencies, and is, above all, a definitely stereo-chemical theory.

To enter into a complete reply to the various critics would occupy too much space in the present volume, and as the publication of the present edition has occupied more than a year on account of the additional matter required—much of which is due to the kind suggestions of the translator—the authors have decided to publish the greater part of their reply to critics in a separate volume to be issued shortly under the title "The Structure of Matter." At the same time it will be noted that the chief criticisms have been met in the present edition, though the following are conveniently noted in the Preface rather than in the text.

A number of critics adopt the remarkable view that the comprehensiveness and unitary nature of the Hexite-Pentite Theory are a disadvantage ! This is specially the case with C. H. Desch[736], Allen and Shepherd[737], C. Doelter ("Handb. d. Mineralchemie"). Yet comprehensiveness and unitary nature are essential characteristics of any *general* theory. No less an authority than Berthollet has declared that the advantage of a general over a special theory is that the former has certain characteristics, which are precisely the ones possessed by the Hexite-Pentite Theory. In Gmellin-Kraut's "Handbuch" and other classical text-books it is admitted that the object of investigation is to produce a complete theory of chemistry from which all natural laws affecting chemical reactions can be predicted or explained. In short,

the comprehensiveness of the Hexite-Pentite Theory is a positive advantage and an indication of its truth.

The earliest opponents to a unitary nature or monism in chemistry were the French investigators Laurent and Gerhardt. Mendelejeff and his associates, on the contrary, are in favour of a monistic theory. Blomstrand, Ostwald, Nernst, Markownikoff and many other well-known chemists have often pointed out the fallacy of the conception of the existence of molecular compounds, and these scientists are therefore in favour of a unitary view. One of the reasons why a portion of the present work was granted a prize by the Faculty of the University of Göttingen was that in it the investigation leads to a unitary conception of the silicates.

One of the most valuable features of the Hexite-Pentite Theory is that it effectively disposes of the necessity for any dualistic conception of matter.

The classification of matter into *chemical compounds* and the so-called *isomorphous mixtures* or *solid solutions*, as is so commonly done at the present time, leads to the conclusion that there are some exceptions to natural laws. Yet when an exception is found to a natural law this is only an indication that the terms in which the law is expressed must be altered so that it may include the apparent exception. Where this cannot be done the "law" must be regarded as imperfectly understood. As Spinoza has remarked, "No sane man will believe that Nature is limited in her powers and that natural laws are of limited and not of general application." The correctness of Spinoza's teaching is clearly shown by the small results which have been obtained from the application of the dualistic or pluralistic theory of matter, i.e. by regarding certain complex compounds as mixtures. Thus, W. J. Müller and J. Königsberger[779], in studying the work of Day and his associates in Washington and of Doelter in Vienna, point out that notwithstanding the skill and expense involved, "the results of these investigations do not appear to be commensurate with the labour involved." Müller and Königsberger attribute this to the absence of analogy between the materials investigated and those used in other branches of chemistry, but the Hexite-Pentite Theory shows that there is an abundance of analogies, and that the true reason for the paucity of results of theoretical value from the Washington and Vienna Institutes is to be found in the erroneous pluralistic view of matter which is held by those in charge.

The constitution of Portland cement has been the subject of investigation for nearly a century, without any definitely satisfactory result. This is due to precisely the same cause—the persistent maintenance

of a pluralistic or mixture theory and the neglect or repression of all information or suggestions to the contrary. The attitude of many supporters of the mixture theories of Portland cements is far from scientific, and notwithstanding the abundance of proof of a chemical nature in favour of the Hexite-Pentite Theory, those in favour of a pluralistic conception of chemical substances still pin their faith to the very slender microscopical evidence on which their theories are based.

One extraordinary "result" of following out the mixture theory in the case of Portland cement is in the experience of two French engineers —Chatony and Rivot (see p. 156 in the text)—at whose instance extensive maritime works were constructed. The panic amongst French and other constructional engineers which resulted from the destruction of these structures can better be imagined than described!

The pluralistic conception of chemical substances has also been the cause of a number of serious accidents and bad results in medical chemistry. Thus, in the opinion of the authors, the pathology of many diseases such as diabetes, cancer, tuberculosis, etc., must remain very incomplete, and the nature and causes of these complaints must be completely misunderstood, so long as the pluralistic conception of matter is maintained. An interesting example of this is found in the toxic action of certain dental stoppings which are fully described in the following pages. So firmly has the mixture theory been held that the opposition to these toxic cements was almost devoid of results, and this theory still exerts a considerable amount of influence, notwithstanding the fact that the authors have not merely shown the causes of the toxic action, but the way to prevent it, and have placed perfectly satisfactory and non-poisonous dental cements, made in accordance with the Hexite-Pentite Theory, on the market. The continued maintenance of the pluralistic conception of matter in medicine is, therefore, even more dangerous than it is in industry.

Among the various critics, it is pleasing to turn from those who have reviewed the first edition of this book in a careless or partial manner to greater scientists like Wilhelm Ostwald[780], who states, "The authors commenced with an explanation of the constitution of the clays and allied substances, but passed on from one branch of chemistry to another until they have eventually been able to illuminate an astonishingly large number of different facts, all of which are regarded from the same point of view." That so able a chemist as Ostwald should describe the present work in such glowing terms is particularly gratifying to the authors, more especially as Ostwald had the opportunity, as a student of Lemberg's, of knowing the remarkable pains which Lemberg took in the prosecution of his investigations—studies which

have proved invaluable as a source of experimental evidence with which the Hexite-Pentite Theory is in complete agreement. Ostwald even goes so far as to state that "as an observer for many years of the production and development of many scientific theories and works I cannot avoid declaring the present one as most unusual. Let us give a hearty welcome to these young and energetic investigators and assure them that the further results of their work will be watched with the greatest interest."

In this connection it is interesting to recall the regret which Landolt expressed that his friend Kekulé did not live long enough to see this new triumph of his Benzene Theory, for the Hexite-Pentite Theory may be very definitely regarded as an extension and development of the Dalton-Kekulé teaching. In a letter, Landolt also expressed his definite opinion that, sooner or later, the Hexite-Pentite Theory must be taken up by chemists in every branch of the subject. The remarkable results which followed the synthesis of various scents, anæsthetics, dyes, etc.—all of which are primarily due to the Kekulé Theory—are strong evidence in favour of the Hexite-Pentite Theory, for Kekulé's theory is essentially a part of the Hexite-Pentite Theory.

Ehrlich's Side-chain Theory is, in a similar manner, another part of the Hexite-Pentite Theory, and the enormous value of Ehrlich's theory in physiological chemistry is already recognised by specialists in this subject.

It is also interesting to observe that the facts which have led to the Guldberg-Waage Theory are also direct consequences of the Hexite-Pentite Theory.

Even Newton's law of gravitation has an interesting connection with the Hexite-Pentite Theory.

The subject of *colloids*, which is attracting a large amount of attention at the present time, is exceptionally well illuminated by the Hexite-Pentite Theory, and the authors had intended to include a considerable amount of information on this subject in the present work. The amount of space occupied would be so great as to make the present volume inconveniently large, however, and would so seriously delay its publication that this subject must be dealt with in a subsequent volume. The reader's attention is, however, called to the subjects of cements and coloured glasses—discussed somewhat fully in the present volume—for hitherto the constitution of these has usually been explained in terms of colloids. Such an explanation is highly individualistic and cannot be applied to cements or glasses as a whole, so that it cannot be regarded as a really scientific hypothesis. By means of the Hexite-Pentite Theory, on the contrary, the cause of the colour of

certain glasses is explained in a manner precisely analogous to that in certain coloured organic compounds, wherein the colour is known to be due to the arrangement of the atoms.

In preparing this English edition, the authors have had the inestimable advantage of the assistance of a well-known authority on clays and other silicates, and they hereby wish to express their indebtedness to him, not only for the manner in which he has executed the translation, but also for his kindness in making numerous and valuable suggestions and criticisms and for the various additions (printed in smaller type for their better distinction) due to his special knowledge of the subject.

THE AUTHORS.

July, 1913.

THE SILICATES.

Introduction

The Chemistry of Carbon and Silicon

THE remark has frequently been made that, whilst the study of carbon compounds has reached a high state of development, comparatively little attention has been paid to that of other elements. A large number of chemists are engaged in studying the chemistry of carbon because the methods of investigation have been worked out more thoroughly than those for other elements; because the interpretation of the results is clearer, and because many carbon compounds, such as the organic dyestuffs and more recently the artificial scents, have proved to be of enormous technical value.

The majority of chemical theories put forward in recent years are based on the characteristics of carbon compounds and are modified, abandoned, or again become generally recognised, without the chemistry of other elements having any appreciable influence upon them. There can be little doubt that if the study of other elements had reached as high a state of development as that of carbon, not a few facts would have been discovered which would lead to other constitutional formulæ and to fresh hypotheses and theories; it is, indeed, probable that at least as many new laws would be formulated as have resulted from the widespread investigation of the chemistry of carbon. These additional laws and generalisations should be of even greater value, inasmuch as they would be based upon a wider knowledge.

Many industries should derive considerable benefit from the results of a more thorough study of inorganic chemistry, and new products—or even new industries—would probably result. The carbide industry and that of the rare earths owe their existence to an increased study of this branch of chemistry. Other industries such as those concerned in the production of artificial gems, inorganic colours, the manufacture or employment of cement, clay, ultramarine, glass, etc. are capable of extensive development through the application of scientific investigation to the materials used in them.

Whilst carbon has a special interest on account of its being the

essential constituent of all organic substances, its analogue, silicon, should be no less interesting as it forms the chief material in the earth's crust. It probably plays a far more important part in the natural processes of the inorganic world than carbon does in the realm of organic substances. A moment's thought will show the immense variety of chemical reactions and the enormous scale on which they occur in the upper layers of our planet. The form of the earth's surface, the character of the mountain ranges, volcanic eruptions and the phenomena of solution and decomposition are all related to such characteristics of the widely distributed aluminosilicates as their hardness, fusibility, heat-conductivity, resistance to pressure, etc. These characteristics are closely related to the composition and the chemical nature of the elements concerned, particularly silicon. How great an interest a knowledge of the structure of these compounds possesses, is shown by the manner in which mineralogists and chemists study the crystallographic, physical and chemical properties of rocks and by the great variety of theories which have been formulated in order to give some idea of the constitution of these remarkable compounds.

In spite of great intellectual effort and innumerable experiments—only a small proportion of which have been published—which have been made to draw this subject from its obscurity, little progress has been made, and the silicon compounds, in spite of the fact that they occur in enormous quantities and are most widely distributed, must be included amongst those substances of whose constitution very little is known.

For this reason it is thought that a fresh attempt to illuminate this subject by investigating it in a purely experimental manner, as distinct from the more theoretical considerations of other scientists, may not be without value.

Section I

Historical Survey of the various Theories regarding the Constitution of the Aluminosilicates and other Silicon Compounds

THE scientific study of the constitution of the silicates commenced in the first decade of the nineteenth century when Berzelius[1] * Smithson[2] and Döbereiner[3] simultaneously (1811) regarded the silicates as salts of silicic acid or silica. Previous to this, the rôle played by silica was, in spite of the researches by Bergemann, Klaproth, etc., far from clearly understood. The silicates were regarded as complex mixtures of various oxides and as peculiar substances quite distinct from other salts. Very few suggestions as to their true character can be found in the earlier literature; they remained outside the general development of scientific knowledge, as Tachenius—who regarded the silicates as salts of silicic acid—endeavoured to show in the seventeenth century.[4]

Although the suggestion that the silicates are salts of silicic acid or silica was made simultaneously and independently by Berzelius, Smithson and Döbereiner, as already mentioned, the chief credit must be given to Berzelius; Smithson contented himself with stating that minerals do not differ from artificially prepared compounds, and that the composition of the silicates can only be understood by regarding them as salts, and quartz as an acid.

Döbereiner[5] worked on purely speculative lines, and argued that as silica forms salts with bases, the oxide of silicon, SiO_2, should be termed "silicic acid." †

Berzelius expressed himself much less decidedly, though his meaning was equally clear.[6] He stated that when two oxides combined, one must be regarded as electro-negative, and suggested that the nomenclature of such oxides could be distinguished from that of the salts. Several years later he classified silica compounds into bi-silicates, tri-silicates, etc. according to the proportion of oxygen in the silica and the base, and made some very clear suggestions regarding the formation

* References to authorities are given in the Bibliography at the end of this volume.

† The term suggested by Döbereiner, viz. "Kieselsäure," is that used in Germany at the present day, there being no exact equivalent in German to the English word "silica." The word "Kieselsäure" thus represents both "silica" and "silicic acid," the latter term expressing its meaning exactly, though seldom used except where the acid nature of the substance is specially under consideration.—A. B. S.

of the complicated salts of silica. At that time he was so convinced of the acid nature of silica that he believed that no mineralogist acquainted with the chemistry of the period could have the slightest doubt that silica was a true acid. He maintained—as Smithson had done before him—that double salts existed in silicates containing Al_2O_3 and Fe_2O_3, and pointed out the analogous nature of the alums in which silica is replaced by sulphuric acid. He also regarded the spinels as salts in which Al_2O_3 plays the part of an acid. These suggestions were at once accepted by scientists.

By great industry, Berzelius largely extended our knowledge of silicates. The discovery of isomorphism by Mitscherlich and the investigations of Bonsdorff and Rose—two pupils of Berzelius—confirmed their master's theories and made it possible to provide simple formulæ for a number of silicates.

Through the use of a formula—which for silica was written as SiO_3, SiO_2, or SiO—a great simplification occurred, though for the silicates as a whole the expression of the results of chemical analyses by formulæ did not fulfil expectations.[7]

In 1846 Laurent[8] suggested that the silicates are not salts of a single, but of several silicates. He had proved the existence of several tungstic acids and presumed the existence of several silicic acids of different chemical compositions analogous to ortho- and meta-phosphoric acid. This hypothesis was accepted by scientists as soon as the value of the "Type theory" had become generally recognised. Between 1855 and 1865 it was in great favour, and it is still held by some chemists. About the time mentioned, Frémy's work on tin-acids was published, and from this arose the idea of poly-silicic acids and anhydrides, which was readily adopted. This hypothesis has been published at various times and from various points of view by Frémy[9], St. Hunt[10], and Wurtz[11], its clearest and most accurate form being due to Wurtz. Various modifications of it have been used in theoretical investigations by several scientific writers with greater or less effect, and there is in existence a long series of treatises, each more or less independent of the others, forming complex combinations of old and new work, by Wöltzien[12], Golowkinski[13], Odling[14], Streng[15], Lawrow[16], Schiff[17], Bödecker[18], Städeler[19], and others. The chief result of all these researches is to indicate that the theories put forward do not *de facto* suffice to render the constitution of the silicates clear. So far as they are concerned, the problem remains unsolved in spite of the large amount of work done in connection with it.

A great advance was made by Damours[20], who was the first to suggest that the water in many silicates is of the nature of "water of constitution," i.e. it is an integral ingredient of the salt (silicate) itself. The importance of this observation was pointed out by Laurent[21], Bödecker[22], and Rammelsberg[23], and its application has greatly increased the significance of the formulæ of many silicates. More recently, Clarke[24] has endeavoured to explain the behaviour of a

series of hydrous aluminosilicates—the zeolites—at high temperatures by means of structural formulæ.

Many silicate formulæ have been further simplified by the employment of microscopical analysis.[25]

There still remained, however, a very large number of silicates whose constitution cannot be ascertained by means of the numerous investigations and exact analytical methods previously mentioned.

This state of affairs naturally led to further attempts to ascertain the constitution of the silicates, and numerous new theories were formulated. Thus, Wartha[26], Haushofer[27], and Šafařík[28] endeavoured in 1873–4 to explain the chemical nature of the silicates by means of structural formulæ. These attempts, which were based on theories of the structure of carbon compounds, did not lead to any definite result and had no appreciable influence on the development of theories relating to silicates.

The felspar-theory published by Tschermak[29] in the "Transactions of the Vienna Academy," in 1865, on the contrary, was of great importance, but was only accepted by scientists after it had been discussed for several years.* This theory, which assumes that some of the felspars are formed by the mixture of two substances—albite and anorthite—is well supported by a large number of analyses, and was undoubtedly of great value at the time it was introduced. It not only facilitated the systematisation of a large number of analyses, but explained the relationship between certain physical characters and the chemical composition of several silicates.

In Tschermak's theory the purely chemical functions of the silicates are not considered; this is its great weakness, and for this reason this theory was only accepted by scientists for want of a better interpretation of the results of innumerable analyses of felspars. This difficulty existed until quite recently, for in Mineralogy there are a number of similar theories in which the chemical characteristics of the compounds concerned are entirely disregarded, as in the ordinary theories of the chemical nature of Scapolite[30], Mica[31, 32], Tourmaline[33], etc.

Towards the end of the "'seventies" very few ideas on the constitution of silicates were promulgated, the work done at that time being chiefly in the direction of increasing the number of observed facts and improving the "observation material" from which conclusions might be drawn with greater accuracy and safety than hitherto.

Such researches as these made it possible for Vernadsky[34] to publish his interesting treatise on "The Sillimanite Group and the rôle of Aluminium in Silicates." A considerable time before Vernadsky, several authorities had agreed that aluminium in silicates has the characteristics of an acid; some presuming the existence of complex

* Special attention is directed to Reference No. 29 in the Bibliography at the end of this volume.

silicoaluminic acids whilst others believed that aluminium in the aluminosilicates plays the same rôle as silicon. Bonsdorf[35], as the result of investigations on hornblendes containing alumina in which the proportions of SiO_2 and Al_2O_3 vary, reached the conclusion that silicon and aluminium each play the same rôle. Scheerer[36] confirmed this view of Bonsdorff's. The view that aluminium in the natural silicates has an acid character was also held by Berzelius[37], Bödecker[38], and Odling[39].

Wartha[40] was the first to publish this hypothesis in a clear form, but he afterwards paid more attention to structural formulæ and ceased to develop this theory. About the same time, Brauns[41] attributed an acid character to aluminium in natural silicates, but instead of the ordinary formula, Al_2O_3, he preferred AlO_2.

Vernadsky endeavoured to show that aluminium plays the same rôle as silicon in the aluminosilicates and that from the latter complex acids (silicoaluminic acids) may be produced. Earlier observations and experiments on aluminosilicates and the chemical changes occurring in Nature completely confirmed this view. At first, Vernadsky sought to base a chemical classification of the aluminosilicates on his theory, but this could be applied to only a small number of compounds. Most of the aluminosilicates, such as felspar, mica, etc., could not be brought within any scheme he could devise, and though he repeatedly declared that the so-called "mixture theories" have little real value from a chemical point of view, he believed that it was unwise to abandon them.

Vernadsky's[42] structural formulæ have consequently done little towards solving the problem of the constitution of the silicates.

The present theories as to the constitution of aluminosilicates appear, with the exception of that of Vernadsky, to be combinations of older theories. The existence of various ortho-, meta-, and other silicic and poly-silicic acids, and of simple and double salts of these, is generally accepted, and to some extent structural formulæ have been allocated. The theories of Rammelsberg[43], Groth[44], Clarke[45], Tschermak[46], and others are of this kind. Those of Sawtschenkow[47] and, more recently, of Goldschmidt[48], differ somewhat, as they are based on the idea that the above-mentioned silicates cannot be explained by the foregoing theories. The researches of Bombicci[49] and Brauns[50], which are based on purely hypothetical considerations, are quite different from those previously mentioned.

The recognition of the acid nature of clays is rapidly gaining general acceptance. Kaolin behaves in many ways precisely like an acid, displacing carbon dioxide in carbonates, chlorine in chlorides, etc., and Mellor and Holdcroft[708] consider it to be aluminosilicic acid (kaolinic acid). These writers, like Vernadsky, classify the aluminosilicates according to the ratio of Al_2O_3 to SiO_2 and distinguish them as alumino-*mono*-, alumino-*di*-, alumino-*tri*-, alumino-*tetra*-, alumino-*penta*- and alumino-*hexa*-silicates. For instance, they regard nepheline,

$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2$ as a salt of an alumino-di-silicic acid; orthoclase, $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$ as a salt of an alumino-hexa-silicic acid, etc. They also suggest constitutional formulæ for these substances, but without contributing materially to any understanding of the constitution of the aluminosilicates, as explained later.

W. Pukall[704, 710] also refers to the acid nature of kaolin which, when digested on a water-bath for several days with a solution of caustic soda, fixes a large quantity of the soda. He has also observed that kaolin at a temperature of about 950° C. causes the evolution of chlorine from common salt and liberates a compound corresponding to $Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2$. Among other writers who have recently referred to the acid nature of alumina in the aluminosilicates may be mentioned J. Morozewicz[711], who also regards kaolin as a complex aluminosilicic acid.

An observation by Daikuhara[712] is highly confirmatory of the acid nature of alumina in the aluminosilicates. It is well known that silica which has been precipitated from solution and afterwards well washed is neutral to litmus. Daikuhara has examined various hydro-silicates, particularly clays, which are *acid* to litmus and observed that, notwithstanding repeated thorough washing, these silicates completely retained their acidity, no acid passing into the wash-water. If, however, a neutral salt such as potassium chloride, ammonium sulphate or ammonium chloride is added to the clay a soluble acid is immediately produced, the potash or ammonia being absorbed and hydrochloric or sulphuric acid liberated. This is important in connection with another fact established by Daikuhara, viz. that finely divided felspar—which he regards as a neutralised kaolin—on prolonged treatment with an aqueous solution of carbon dioxide produces an acid-reacting silicate which behaves in a manner similar to the clays just mentioned.

Section II

Critical Survey of the Existing Theories of Aluminosilicates

THE following hypotheses or theories have been formulated to explain the constitution of the aluminosilicates:

1. The aluminosilicates are salts of silicon hydrate in which the hydrogen is partly replaced by aluminium and partly by other metals.

2. The aluminosilicates are double salts—silicic salts of aluminium and other metals—and also isomorphous mixtures of these double salts.

3. The aluminosilicates are molecular compounds composed of various chemical compounds which have nothing in common as

regards their chemical nature. The mode of combination between the various components is very labile.

4. The aluminosilicates are isomorphous mixtures of salts of silicic and aluminic acids.

5. The aluminosilicates are double salts of silicic and aluminic acids, or amorphous mixtures of these double salts.

6. The aluminosilicates are, in part, silicoaluminic acids and, in part, the salts of these acids.

Before we criticise these theories in the light of the facts, it appears desirable to make the following statement: The aluminosilicates constitute a single, well-defined class of compounds, the members of which agree in the numerous observable chemical changes which they undergo in Nature (the so-called pseudomorphic processes) and in those of their characteristics which are best studied in the laboratory, such as their synthesis and their behaviour towards reagents and at high temperatures. In these ways the aluminosilicates differ considerably from silicates which are free from aluminium and other sesquioxides. No reaction is known which makes it necessary to place any of these compounds in a special class or to give them a special place in a separate class. They pass into each other or form the same compounds; they all change slowly under the influence of geological processes into one and the same compounds of the kaolin group. In considering these hypotheses we must take special notice of this phenomenon; and in explaining the chemical nature of the compounds under consideration, only those hypotheses or theories should be employed which make it possible to indicate the composition of these compounds in a uniform manner and to exclude those silicates which show important differences of character. That hypothesis or theory which agrees most closely with the facts and is free from obvious disadvantages must be regarded as the one which approaches nearest to the truth.

(*a*) Critical Examination of the First Hypothesis

According to the first hypothesis the aluminosilicates are silicohydrates in which one part of the hydrogen is replaced by aluminium and another part by other metals.

This theory contradicts the following facts:

1. The relation between aluminium and the other metals contained in these compounds remains constant no matter how soon the reaction of the double decomposition is interrupted.

2. No reaction is known whereby it is possible to produce a hydrate of silicic acid from the aluminosilicates and from this hydrate to reproduce the original substance, i.e. the aluminosilicate. The separation of silica by means of strong acids is always accompanied by a complete destruction of the whole compound. The replacement of the metal by hydrogen usually occurs in such a manner that only those metals can be substituted which are capable of forming oxides of

the R''O and R'_2O type, the aluminium remaining unaffected; from these intermediate products—which appear to be acid salts of aluminium—it is easy to regain the original compounds. The replacement of aluminium by hydrogen without affecting the other metals has not yet been accomplished.

3. No instance is known in which all the hydrogen of the hypothetical silicic hydrate can be replaced by a single metal, though one metal may be substituted for one portion of it and another metal for the remainder. Thus, the transformation of $Si\,Al\,NaO_4$ into $Si\,Na_4O_4$, or the reverse, by means of a double decomposition is impossible.

4. If it is desired to use this hypothesis in the study of the aluminosilicates and to apply it to all of these compounds, it is necessary to conceive the existence of highly complex and improbable silicic hydrates or of basic salts. Even then, this hypothesis affords no assistance for many compounds, such as the sapphires.

5. If this hypothesis is accepted, the simple reactions which occur with these compounds cannot be explained. For example, the transformation of one aluminosilicate into another has frequently been observed, the ratio of alumina to the R''O and R'_2O oxides remaining unchanged and only the ratio of silica to these oxides varying; e.g. reactions in which an increase or diminution of SiO_2 occurs. Such reactions are by no means uncommon; orthoclase, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ easily passes into leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$; and later into muscovite, $K_2O \cdot H_2O \cdot 2Al_2O_3 \cdot 4SiO_2$. Analogous changes are the transformation of albite into kaolin and mica, the formation of analcime $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$ from nepheline; the conversion of analcime into muscovite and the artificial production of it from orthoclase, albite and kaolin; the transformation of andalusite, $Al_2O_3 \cdot SiO_2$ into muscovite[51], the conversion of kaolin into analcime by means of sodium silicate[52], the formation of kaolin from nepheline[53], the conversion of eläolite, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ into natrolite[54], $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$, into analcime[55] and into hydronephelite[56], $Na_2O \cdot H_2O \cdot 2Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$; and in the passage of muscovite into leucite by the action of SiO_2 in the presence of alkali carbonates[57]. These reactions, selected from a much larger number, are quite inexplicable by the first hypothesis.

It is, therefore, scarcely conceivable that those constitutional formulæ of the aluminosilicates which are based on the first hypothesis are in accordance with the facts.

Recently, several mineralogists, including Brögger[58], Clarke[59], Groth[60], endeavoured to use the first hypothesis by presuming the existence of several complex aluminium radicles such as AlCl, AlF_2, AlO, etc., which replace metals and can form RO oxides. Unfortunately, no chemical reactions are known in support of this hypothesis, which is entirely based on the arrangement of the silicates according to their crystalline form.

Moreover, this modified hypothesis gives little or no explanation

of the constitution of the chemical compounds just mentioned, and, all things considered, it must be admitted that the first hypothesis does not explain the reactions to which reference has been made.

(b) Critical Examination of the Second Hypothesis

The second hypothesis (that the aluminosilicates are double salts of aluminium and other metals and that they also comprise isomorphous mixtures of these double salts) is one of the oldest. It was originated by Berzelius and Smithson.

The following objections to this hypothesis require consideration :

1. Any reaction in which the proportion of silica in the compound varies whilst the proportion of aluminium to base remains constant is inexplicable.

2. This hypothesis requires the existence of very stable double salts of different silicic acids, or of double salts composed of both normal and basic salts. It cannot be said that the production of double salts from salts of different basicity or acidity is impossible, as our knowledge of the double salts is far from complete.

The existence of such salts is, however, highly improbable and if this hypothesis were correct it would necessitate the placing of such salts in a class by themselves, as, amongst all the substances which have been investigated, no such double salts have been observed.

3. How is it possible to term compounds having the general formula:

$$R_2O \cdot Al_2O_3 \cdot SiO_2$$

double salts ? These compounds occur in Nature and may also be prepared artificially. As naturally occurring minerals : $CaO \cdot 2\,Al_2O_3 \cdot 2\,SiO_2 \cdot H_2O$ (Margarite[61]) and $MgO \cdot Al_2O_3 \cdot SiO_2$ (Prismatine[62]) may serve as examples of this group. Artificially prepared $K_2O \cdot Al_2O_3 \cdot SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot SiO_2$ form typical synthetic products.[63]

All these compounds are closely related to compounds in other groups ; thus $K_2O \cdot Al_2O_3 \cdot SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot SiO_2$ readily change into $K_2O \cdot Al_2O_3 \cdot 2\,SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2$ respectively, and inversely they may both be obtained from kaolin.[64] Margarite is closely related to the micas and is not infrequently formed from them.[65] Prismatine changes into a hydrous silicate (Krypolite) which, according to this hypothesis, must be regarded as a double salt and in the form of phlogopite may be obtained artificially.[66]

There is clearly a genetic relationship between the various aluminosilicates, but to regard them as double salts it would be necessary to provide a special space in the scheme of classification, as there are many compounds of this group (which can never be termed double salts) for which no provision is made.

4. The fact that compounds which, from the point of view of those who accept this hypothesis, are very complex in structure are found

on experiment to be very stable, is puzzling. Thus the group $R_2O \cdot Al_2O_3 \cdot 2\,SiO_2$, into which practically all other aluminosilicates may be readily converted, is characterised by its exceptional stability. Those who accept this hypothesis regard the compounds of this group as double salts, having the general formula :

$$R'_2SiO_3 + Al_2SiO_5 \quad \text{or} \quad R'_2SiO_3 + R'_6SiO_5,$$

i.e. as normal salts of meta-silicic acid with a basic salt of some other silicic acid. It is scarcely conceivable *a priori* that the representatives of the most stable substances of the whole class of aluminosilicates are to be found in compounds of this composition.

5. To the view that the aluminosilicates are double salts there is also the following objection: The term "double salt" is by no means clearly defined and gives but little definite information as to the nature of the compounds to which it is applied. This term should, therefore, be used more cautiously than is sometimes the case and should only be applied to those substances of which the mode of formation from their constituent salts is clearly ascertainable. For example, it is quite correct to term the compound $K_2Mg(SO_4)_2 \cdot 6$ aq. a double salt, because it can be produced directly from the two constituent salts, K_2SO_4 and $MgSO_4$. But can such syntheses be observed in the case of aluminosilicates ? Can any analogous reaction be found among the innumerable compounds of silica ? The syntheses which have actually been effected suggest the exact opposite of the second hypothesis and are most puzzling when an attempt is made to apply it to them. No syntheses in support of this hypothesis have yet been made.

It is impossible by this hypothesis to explain the formation of compounds such as analcime, $Na_2O \cdot Al_2O_3 \cdot 4\,SiO_2 \cdot 2\,H_2O$ (which is produced[67] by the action of Na_2SiO_3 on $NaAlO_2$), or of other aluminosilicates which are obtained from silicates and aluminates.[68] In these compounds aluminates are found, but no aluminium silicates, a circumstance which is quite contrary to the conception of aluminosilicates as double salts.

(*c*) Critical Examination of the Third Hypothesis

According to the third hypothesis, the aluminosilicates may be regarded as molecular compounds, i.e. compounds in which the unit of combination is a molecule and not an atom.

This conception of the constitution of natural silicates has chiefly been favoured by Bombicci[69] and V. Goldschmidt, others only having applied it to a few specific cases, as Mallard[70], who used it to explain the constitution of chondrodite.

Some silicates are undoubtedly molecular compounds, particularly those silicates which contain water of crystallisation. Some researches of Lemberg[71] and Doelter[72] indicate that cancrinite is a molecular compound and other investigations by Lemberg and Thugutt lead to

the conclusion that the sodalites are also molecular compounds. Other natural silicates appear to confirm this view, so that at first sight it seems as if this hypothesis would enable the facts to be satisfactorily explained; in reality, the facts are in direct contradiction to the theory. A closer investigation shows that any agreement between fact and theory which may occur is a coincidence due to the indefiniteness of the latter; this indefiniteness makes a large number of suppositions possible. Many facts, whilst not exactly in opposition to it, cannot be used in support of this theory because they cannot be predicted from it. For this reason, this hypothesis has not the value of a true scientific theory or "law of Nature," one essential feature of which is the facilities it offers for the prediction of properties of substances from a knowledge of their constitution.

The very indefiniteness of the term "molecular compound" allows the formulation of innumerable theories and makes it extremely difficult to decide which of these are of value and which are merely ingenious speculations. To make this clearer it may be assumed for the moment, that the compound

$$K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$$

is composed of two or more molecules. In selecting these there is an enormous number of possible molecular compounds to choose from, all of which correspond to the formula of orthoclase given above. For instance, there are

1. $K_2Al_2Si_2O_8 + 4\,SiO_2$,
2. $K_2SiO_3 + Al_2SiO_5 + 4\,SiO_2$,
3. $K_2SiO_3 + Al_2Si_3O_9 + 2\,SiO_2$, etc.

ad infinitum.

It is clear that from the formula for orthoclase, taken as an example, as many different molecular compounds can be written out as there are mathematical combinations of symbols of the elements available. If one of these hypothetical formulæ is found not to represent the characteristics of the substance under consideration, a second, third, fourth, and so on, is substituted. The matter is still further complicated by the indefiniteness of the term "molecular compound" as used by different writers; an indefiniteness which enables those who use it to indulge in all manner of speculations.

Broadly speaking, there is no definite means of deciding whether a given substance should be regarded as a molecular or as an atomic compound. Usually, those substances are regarded as molecular compounds which cannot be otherwise understood,[73] the subjective conception of each individual scientist being the factor which determines whether he will regard a given chemical compound as molecular or atomic. Some chemists regard the so-called "double salts" as molecular compounds, whilst others regard some of these salts as atomic and the remainder as molecular compounds. This shows that great caution is necessary in using these terms for the solution of

theoretical questions. In Science, it is only in rare cases that a theory can be used which, on account of its indefiniteness and lack of clearness, does not possess all the requirements of a scientific hypothesis.

If aluminosilicates are molecular compounds they must show definite properties characteristic of their constitution. This is not the case. Molecular compounds are formed of chemical compounds of definite composition (Molecules) and must necessarily be less stable than atomic compounds, as the force which binds molecules together must, naturally, be weaker than that which unites atoms to form molecules. Under many conditions, such as solution in water, or when under the action of heat or chemicals, molecular compounds split up into their component molecules. Many aluminosilicates show a high degree of stability; some can be dissolved and afterwards converted into the solid state without undergoing the least decomposition (e.g. $CaO \cdot Al_2O_3 \cdot 2\,SiO_2$, $Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2$, etc.). The decomposition-products formed when aluminosilicates are heated are usually complex and can, more reasonably, be termed molecular compounds. Thus, the majority of the calcareous aluminosilicates form $CaO \cdot Al_2O_3 \cdot 2\,SiO_2$, and analogous compounds.[24] The reactions of these apparent components take no part in the chemical reactions of the aluminosilicates.

The indefiniteness of the theory here criticised and the absence of facts in support of it show definitely that it does not suffice to give a clear idea of the constitution of the aluminosilicates. This very indefiniteness of the hypothesis is also a reason why it is impossible to find many facts which can be used in direct disproof of it.

(d) Critical Examination of the Fourth and Fifth Hypotheses

According to the fourth hypothesis, aluminium and silicon both play the part of acid forming elements, and the aluminosilicates are regarded as isomorphous mixtures of aluminates and silicates. As no facts are available which show that, in natural silicates, aluminium plays, to some extent, the part of acid- and, to some extent, that of a base-forming element, it may be assumed that in the silicates the aluminium is present as aluminic acid and has not replaced part of the hydrogen of the silicic hydrate.

This view renders the constitution of a large number of aluminosilicates quite inexplicable, particularly those with less base than is required by the number of hydroxyl groups of the corresponding silicic and aluminic hydrates, e.g. $K_2O \cdot Al_2O_3 \cdot 4\,SiO_2$, $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$. This hypothesis also fails to explain the proved formation of silicates containing alumina by the decomposition of aluminosilicates and the invariable occurrence of alumina and silica in the products of the reaction. Indeed, this hypothesis indicates precisely that the contrary should be expected, viz. ready decomposition into aluminates and silicates, as the valencies of the constituents of isomor-

phous mixtures (of aluminates and silicates) are naturally weaker than those of the atoms which form the components of the mixtures.

The confirmation of this hypothesis by the synthesis of aluminosilicates from aluminates and silicates is more apparent than real, as the ratio of base : aluminium : silica in the products of the reaction is quite different from that which would be found if aluminates and silicates could form isomorphous mixtures. Thus, analcime, $NaAlSi_2O_6 \cdot aq.$ and similar substances are producible from Na_2SiO_3 and $NaAlO_2$. Moreover, it has never been proved that the salts of aluminosilicic acids are isomorphous, and to attribute this character to them is pure hypothesis. A similarity is often observed in the forms of crystals, e.g. chrysoberyl and olivine, but except for this single resemblance no evidence has been given of isomorphism. No actual observations of isomorphous mixtures produced directly from aluminates and silicates have ever been published.

But little importance can, therefore, be attached to the fourth hypothesis, as it is only applicable in special cases (such as those investigated by Rammelsberg[75], Knop[76], and others) and has never been of general application to the study of the constitution of the aluminosilicates.

The foregoing hypothesis may be somewhat modified so as to indicate that isomorphous mixtures of aluminates and silicates and isomorphous mixtures of double salts having aluminates and silicates as their components, may be formed along with the aluminosilicates. This leads directly to the fifth hypothesis. Yet, even in this form, the facts do not agree with the theory. The invariable presence of aluminium and silica appears to be inexplicable—the contrary appears to be more probable—the reaction products must, if this hypothesis is correct, contain either silicon *or* aluminium, but not silicon *and* aluminium in one and the same product.

According to the fourth and fifth hypotheses, those aluminosilicates which consist exclusively of SiO_2 and Al_2O_3 appear to occupy a special position, yet between them and other aluminosilicates an undoubtedly genetic relationship is shown to exist by the ease with which they can be transformed into one another. The first contain no alkali and cannot, for that reason, be regarded as isomorphous mixtures or double salts of aluminates and silicates. If, however, these substances are to be regarded as aluminium salts of silicic acid, the aluminosilicates must, under other circumstances or in other cases, be shown to be so constituted that, in them, the aluminium has replaced the water of the silicic hydrate; yet this, if true, destroys the fourth and fifth hypotheses. The compounds last mentioned cannot be regarded as isomorphous mixtures of Al_2O_3 and SiO_2, as the isomorphism of these compounds still remains to be proved; moreover, the existence of an invariably simple ratio of alumina to silica is also opposed to such an isomorphism.

Similarly, the constitution of those aluminosilicates which contain

water in addition to Al_2O_3 and SiO_2 is very puzzling if studied in connection with these hypotheses.

Hence, the fourth and fifth hypotheses cannot be used to explain the constitution of the aluminosilicates.

(e) Critical Examination of the Sixth Hypothesis

According to the sixth hypothesis, the aluminosilicates are complex acids or the salts of complex acids. They are, therefore, analogous to the silicotungstates, arsenomolybdates, silicomolybdates, phosphomolybdates, etc. All the substances just mentioned have been placed in a new group by Wolcott Gibbs[77], though some facts which indicated the existence of complex acids were known long before Gibbs' work was published.

Before making any statement as to the value of this hypothesis in the study of the constitution of the aluminosilicates the following questions must be clearly answered :

I. To what results do previous chemical and physico-chemical researches on the complex acids and their salts lead, as regards their chemical nature ?

II. What theories have been formulated with regard to the chemical constitution of the complex acids and what is the value of these various theories ?

With regard to the first question the following statement may be made :

(a) The properties of the complex acids producible from a series of acids such as tungstic, molybdic, vanadic, phosphoric, arsenic, silicic, antimonic, and other acids by the combination of two or more of these acids (as silicic and tungstic, phosphoric and molybdic, etc.) in definite proportions do not completely coincide with the sum of the properties of their components.

(b) The acidity of the complex acids is seldom equal to that of the separate acids from which the complex one has been formed.

(c) Any given acid can usually unite in variable but simple proportions to form several complex acids.

(d) The complex acids can exist either in the free state or as salts.

(e) When complex acids take part in a double decomposition, no separation of the component acids occurs. The latter are found in the new product in the same proportion as they were in the original complex acid.*

(f) The conversion of one complex acid into another, composed of the same constituent acids, is easily effected by splitting off one of the acids in the form of a salt or in the free state. Thus, the conversion of one phospho-tungstic acid into another is accomplished by the removal of tungstic acid or one of its salts.

* In other words a complex acid acts as a single acid and not as a mixture of two or more separate acids. - A. B. S.

(*g*) From the corresponding anhydrides a series of complex radicles may be produced, the ratios of the constituents of the anhydrides being always simple.

(*h*) Great difficulties are experienced if such compounds as the silicotungstates, phosphotungstates, etc. are classified in accordance with Ostwald's[78] definition of double salts, and if any attempt is made to divide true complex acids into two groups according to their behaviour in aqueous solution. The recent physico-chemical study of these compounds—made with a view to ascertaining their constitution[79]—has shown that whilst some dissociate, when in aqueous solution, into their components, others are quite stable. The former, according to Ostwald's classification, must be regarded as "double salts" and the latter as "complexes." In some cases, as (1) when a "double salt" contains alkali or (2) with certain proportions of acid and alkali, the use of the term "double salt" is permissible. With many of these compounds this is not the case, e.g. free acids and those which contain a much larger proportion of one of the acids than of the other. For instance, how is it possible to represent the free acid

$$3\,H_2O \cdot P_2O_5 \cdot 24\,WO_3,$$

as a double salt? Yet the physico-chemical researches of Sobolew[80] (dialysis, electrical conductivity, etc.) have shown that in aqueous solution it dissociates into phosphoric acid and metatungstic acid and that its salts are equally unstable in the presence of water.

The division of the compounds under consideration into two groups according to their behaviour when in aqueous solution does not appear to be satisfactory. On the contrary, the experimental results make it appear far more probable that all the compounds in this group are of analogous constitution, though they vary in their stability when in aqueous solution. The following facts appear to confirm this view:

1. W. Asch[776] has shown by means of a physico-chemical investigation (dialysis, electrical conductivity, determination of molecular weight, etc.) of the silico-molybdate

$$2\,R'_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot aq.,$$

that in these compounds the silicic and molybdenic acids form a complex ion. This is confirmed by the production (by the same investigator) of readily soluble barium and calcium salts of the same series, having the general formula

$$2\,R''O \cdot SiO_2 \cdot 12\,MoO_3 \cdot aq. \quad (R'' = Ba, Ca),$$

and acid salts with a composition corresponding to:

$$1.5\,R'_2O \cdot 0.5\,H_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot aq. \quad (R' = K, Na).$$

2. D. Asch[777] has prepared compounds with the general formula

$$2\,R'_2O \cdot 2\,SO_2 \cdot 5\,MoO_3 \cdot aq. \quad (R' = K, Na, NH_4),$$

by the action of sulphurous acid on the alkalies of the paramolybdates. These compounds, unlike the silicomolybdates, are very unstable in water, so that the conversion of the alkali-salts just mentioned into the corresponding salts of the alkaline earths appears to be impossible on account of the decomposition of the latter in water. Only by the use of concentrated alkali-paramolybdate solutions saturated with SO_2 gas, together with the salts of the alkaline earths, was it found possible to prepare readily soluble salts of the alkaline earths corresponding to

$$2\,R''O \cdot 2\,SO_2 \cdot 5\,MoO_3 \cdot aq. \quad (R'' = Ba, Sr, Ca).$$

Consequently, there can be no doubt that the sulphurous molybdates — in spite of their ready decomposition when in aqueous solution — must, on account of the manner in which they form readily soluble salts of the alkaline earths, be regarded as salts of a complex sulphomolybdic acid with the formula

$$2\,H_2O \cdot 2\,SO_2 \cdot 5\,MoO_3 \cdot aq.$$

It is here assumed that the compounds under consideration may be regarded either as free complex acids or their salts, some of these substances being stable in aqueous solution whilst the remainder are more or less unstable.

An answer to the questions (p. 15) concerning the previous theories of the constitution of complex acids and their salts may now be given.

It should be observed that most investigators of these complex acids and their salts have been content to accept the chemical composition without making the smallest effort to theorise on the chemical nature of these compounds. Although the number of these substances is somewhat large, the theories of their constitution are comparatively few, and even these are not free from objections. Amongst them, structural formulæ are of importance and have been employed by several investigators to indicate the chemical nature of several complex compounds. Thus, Fremery[77] endeavoured to represent by structural formulæ the arsenotungstates he prepared. Later, Friedheim[84], Blomstrand[85], Kehrmann[86], Sprenger[87], Michaelis[88] and others endeavoured to follow Fremery's example and to apply analogous structural formulæ to quite different substances. Notwithstanding the fact that the structural formulæ of Blomstrand and Friedheim are analogous, the theories of these two investigators are quite distinct.

Blomstrand[89] compares the ability of the acid anhydrides to combine in various proportions to form complex anhydrides, with that of those salts of cobalt, rhodium, platinum and gold which can combine with ammonia in such a manner as to form "chains" containing $1\,NH_3$ to $3\,NH_3$.

He suggests the following equations to show the combination of ammonia with the metallic salts mentioned :

$$MCl + NH_3 = MNH_3Cl,$$
$$MCl + 2\,NH_3 = MNH_3 \cdot NH_3Cl, \qquad \text{etc.}$$

He regards the formation of the following complex acids as analogous:

$$OX \equiv (OH)_3 + \ \ OMO_2 = OX \begin{array}{l} OMO_2OH \\ (OH)_2 \end{array}$$

$$OX \equiv (OH)_3 + 2\,OMO_2 = OX \begin{array}{l} OMO_2 \cdot OMO_2OH, \\ (OH)_2 \end{array} \quad \text{etc.}$$

He considers that what occurs is the automatic opening of the atomic complex and the introduction of the new group, member for member, whenever this is possible without changing the general character of the whole substance.

Friedheim[90] regards the course of the reaction in the formation of complex acids in an entirely different manner. For instance, he represents the first stage of the reaction of molybdic acid on NaH_2AsO_4 as a combination of the molybdic acid with the base of the arsenic salt as follows:

$$2\,OAs\begin{array}{l} (OH)_2 \\ ONa \end{array} + MoO_3 + aq. = 2\,OAs(OH)_3 + Na_2MoO_4$$

$$2\,OAs\begin{array}{l} (OH)_2 \\ ONa \end{array} + 2\,MoO_3 + aq. = 2\,OAs(OH)_3 + Na_2Mo_2O_7, \text{ etc.}$$

In addition to these molybdates, acid molybdates will also pass into solution, thus:

$$HO \cdot MoO_2 \cdot ONa,$$
$$HO \cdot MoO_2 \cdot OMoO_2 \cdot ONa,$$
$$HO \cdot MoO_2 \cdot OMoO_2 \cdot OMoO_2 \cdot ONa, \text{ etc.}$$

These are unstable and unite with the free arsenic acid with loss of water:

$$OAs\begin{array}{l} O\,|\,H \quad HO\,| \cdot MoO_2 \cdot ONa \\ OH \\ OH \end{array}$$

$$OAs\begin{array}{l} O\,|\,H \quad HO\,| \cdot MoO_2 \cdot OMoO_2 \cdot ONa \\ O\,|\,H \quad HO\,| \cdot MoO_2 \cdot OMoO_2 \cdot ONa, \\ OH \end{array} \quad \text{etc.}$$

Provided that the hydroxyl groups of the acid $OX \equiv (OH)_3$ do not split off automatically with formation of water, the hydrogen of these hydroxyl groups may be replaced by R, the following examples being theoretically possible:

$$OAs\begin{array}{l} OMoO_2 \cdot OMoO_2 \cdot ONa \\ ONa \\ ONa \end{array}$$

$$OAs\begin{array}{l} OMoO_2 \cdot OMoO_2 \cdot ONa \\ OMoO_2 \cdot OMoO_2 \cdot ONa \\ ONa \end{array} \quad \text{etc.}$$

The foregoing structural formulæ are open to the following objections:

1. It appears as if the acidity of the complex molybdates or tungstates is quite independent of the amount of metallic acid (molybdic

or titanic acid) in the complex and is only influenced by the atomicity of those substances with which the metallic acids combine to form a complex. Thus, Pufahl[91] has decomposed a compound of the series

$$3\ R_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot aq.,$$

with silver or thallium salts, and has produced

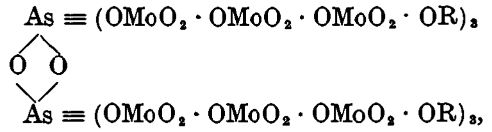
$$6\ Ag_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot aq., \text{ and}$$
$$6\ Tl_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot aq.$$

These compounds contain twice as much base as is theoretically possible.

As Friedheim writes the structural formulæ of the compound

$$3\ R_2O \cdot As_2O_5 \cdot 18\ MoO_3$$

as



which is analogous to the structural formula previously mentioned, he must place the compounds with $6\ R_2O$ in a separate class on account of their proportion of base. He denotes the constitution of such substances as molecular, i.e. he attempts an explanation which, on account of its confused nature, is no explanation at all.

The number of such compounds with a high proportion of base is somewhat large and it is sufficient to mention the following:

(*a*) $6\ R_2O \cdot As_2O_5 \cdot 18\ MoO_3$ [92]
(*b*) $4\ R_2O \cdot B_2O_3 \cdot 12\ WoO_3$ [93]
(*c*) $4\ R_2O \cdot SiO_2 \cdot 12\ WoO_3$ [94]
(*d*) $7\ R_2O \cdot V_2O_5 \cdot 12\ WoO_3$ [95], etc.

To agree with Friedheim's and Blomstrand's theory, the series (*a*), (*b*) and (*d*) can at most contain $3\ R_2O$ and (*c*) only $2\ R_2O$! There is no real reason for placing all these compounds in a separate class, for neither in their properties nor in their mode of formation do they differ from those from which the above structural formulæ were derived.

2. Another weakness of the hypotheses of Blomstrand and Friedheim is that they do not permit of deductions being made in connection with the compounds of the complex acids containing the elements just mentioned, and that the composition of only a relatively small number of the compounds in this class can be represented structurally in the way they suggest.

Moreover, there cannot be sufficient evidence for the proposed structural representation, as, for the majority of these compounds, these two investigators have been contented with the use of empirical formulæ and have not made the smallest attempt to determine their

constitution. This is probably due to the complexity of many of these compounds. Thus, no hypotheses have been formulated for compounds containing 15, 16, 17, 20 and 22 RO_3 (R=Mo, W) to one molecule of X_2O_5 (X=As, P, Vd). Some of these compounds have been prepared from substances to which the structural formulæ apply and their molecular arrangement is then of interest. Thus, Sprenger[96], working with a barium salt of the series $P_2O_5 \cdot 24\,WO_3$ and $Ba(OH)_2$ according to the equation

$$3\,BaO \cdot P_2O_5 \cdot 24\,WO_3 + 6\,Ba(OH)_2$$
$$= 7\,BaO \cdot P_2O_5 \cdot 22\,WO_3 + 2\,BaWO_4 + 6\,H_2O,$$

obtained a member of the series $P_2O_5 \cdot 22\,WO_3$—a reaction which admits of no explanation in terms of the above theory !

Kehrmann and Freinkel have prepared other compounds of this series, viz. :

1. $3\,BaO \cdot 4\,Ag_2O \cdot P_2O_5 \cdot 22\,WO_3$ aq, and
2. $7\,K_2O \cdot P_2O_5 \cdot 22\,WO_3$ aq.

Kehrmann[97] has also prepared from the compound 2, by means of hydrochloric acid and potassium chloride, a crystalline substance with the formula

$$5\,K_2O \cdot P_2O_5 \cdot 17\,WO_3.$$

All these compounds, of which only a small number have been mentioned, can only be explained with great difficulty, and in many cases are quite inexplicable, by the above-mentioned theories of Blomstrand and Friedheim.

3. Structural formulæ are of special value when definite characteristics of the substances they represent can be deduced from them. In this direction the structural formulæ proposed by Friedheim have not been of much service. For instance, the compounds[98]

$$2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3, \text{ and}$$
$$4\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3,$$

which are formed by the action of vanadic acid on potassium, sodium or ammonium paratungstate, are chiefly distinguished from each other by their characteristic behaviour towards acids. Compounds of the type

$$2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3$$

liberate tungstic acid on treatment with hydrochloric acid, but no such separation is observable, when compounds of the type

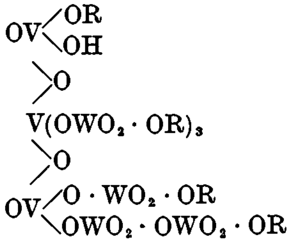
$$4\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3$$

are similarly treated.

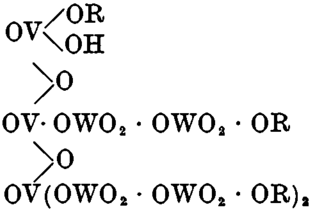
Friedheim represents the structure of these two series as follows :

1. $(2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3 \cdot \tfrac{1}{3}aq.)\,1\tfrac{1}{2} = \tfrac{1}{2}\,H_2O \cdot 3\,R_2O \cdot 1\tfrac{1}{2}\,V_2O_5 \cdot 6\,WO_3$
2. $(4\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3 \cdot aq.)\,\tfrac{1}{2} = \tfrac{1}{2}\,H_2O \cdot 2\,R_2O \cdot 1\tfrac{1}{2}\,V_2O_5 \cdot 6\,WO_3$

1.



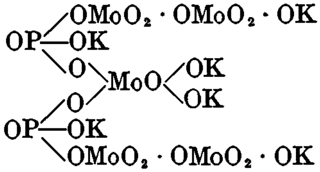
2.



Yet from these somewhat complicated formulæ it is impossible to infer the different behaviour of these two substances to acids, and Friedheim is again compelled to resort to a molecular representation.* The compound[100]

$$3\,K_2O \cdot P_2O_5 \cdot 5\,MoO_3$$

appears to be an exception. It is regarded by Zenker and Blomstrand as molecular, but as atomic by Friedheim, who represents it as



This structural formula shows that one-third of the potassium should behave differently from the remaining two-thirds. This agrees with the behaviour of this substance towards dilute nitric acid, in which one-third of the potassium atoms are more easily separated than the others. This is, however, quite unusual.

Friedheim and his associates also formulated other theories respecting the complex acids and their salts. For instance, they sought to explain their formation by reference to that of the double salts,[101] but this hypothesis is by no means free from objection. The facts mentioned under *h* (p. 16) in the description of the general characteristics of complex compounds are quite opposed to it, and any attempt to apply Friedheim's hypothesis to the chief members of this group is sure to meet with many serious difficulties and contradictions. How is it possible, for example, to use this theory to explain the nature of compounds containing a large proportion of anhydride such as the previously mentioned silicomolybdate

$$2\,R_2O \cdot SiO_2 \cdot 12\,MoO_3$$

or the corresponding silicotungstate? In such a case it is necessary to assume the existence of purely hypothetical molecular compounds.

* Since the above was written Friedheim[99] has abandoned the use of the formulæ 1 and 2 and now uses the atomic arrangement shown below.

The free acids are a source of other difficulties, for how can the constitution of the phosphotungstic acid

$$3\,H_2O \cdot P_2O_5 \cdot 24\,WO_3$$

be represented ?

Friedheim suggested that such free acids contain an anhydride with the character of a base, from which it would follow that the so-called acid is really a salt. Thus, he regarded the compound

$$2\,H_2O \cdot P_2O_5 \cdot V_2O_5$$

as a salt of phosphoric acid,[102] namely

$$PO \begin{cases} (OH)_2 \\ O(VO_2) \end{cases}$$

and an analogous compound,

$$Na_2O \cdot P_2O_5 \cdot 2\,V_2O_5,$$

from which the first may easily be prepared, as a double salt of a vanadium salt of phosphoric acid and a sodium salt of vanadic acid, viz.

$$R_2O \cdot P_2O_5 \cdot 2\,V_2O_5 = R_2O \cdot V_2O_5 + V_2O_5 \cdot P_2O_5.$$

Such a classification is obviously confusing; whenever the analytical results are expressed as formulæ indicative of double salts, the compounds must be similarly represented, or—if double salts are excluded—the formulæ have another meaning and represent either molecular compounds, whose components are hypothetical, or—in the case of free acids—compounds in which one of the two anhydrides is regarded as a base.

Summary

In summarising the arguments for and against these theories with regard to the constitution of the aluminosilicates, it should be observed that the sixth hypothesis (that the aluminosilicates are complex acids and the salts of such acids) explains a whole series of reactions which are quite inexplicable by the other hypotheses (with the exception of the "molecular compound" theory by which "everything" can be explained) and that most of the best-known chemical reactions involving aluminosilicates are in agreement with it.

It is now clear that :

1. The splitting off or addition of SiO_2 is a sign of the formation of complex anhydrides and analogous compounds.

2. The simultaneous presence of SiO_2 and Al_2O_3 in the products of the aluminosilicates and the easy conversion of one aluminosilicate into others are comparable to the analogous reactions of phosphotungstates, phosphomolybdates, etc.

3. The ratio $SiO_2 : Al_2O_3$ remains unaltered in reactions involving double decomposition and that no replacement of aluminium by elements capable of forming oxides of the $R''O$ or R'_2O type has been observed.

4. There is a genetic relationship between all aluminosilicates, and that they can be converted into each other.

5. Most of the aluminosilicates are convertible into stable compounds by the action of geological forces.

6. The reactions of a geological nature are analogous for all the silicates; those which contain no Al_2O_3, etc. (but are almost entirely composed of SiO_2) under atmospheric influences form silicic hydrates (opals), whilst the salts of the complex aluminosilicic acids are, under similar conditions, converted into the hydrates of the complex aluminosilicate radicles (kaolins).

7. Highly aluminous aluminosilicates (sapphirin) as well as those low in alumina (petalite) are known to exist.

There is also a large number of facts indicative of the acid character of aluminium in the aluminosilicates, as previously mentioned. In some highly aluminous slags, salts of aluminic acid (aluminates) are known to be formed at high temperatures, and silica appears to be unable to displace the aluminic acid from these compounds.[103] The simultaneous formation of salts of silica and alumina, even in the presence of an excess of free silica, has been observed; this fact clearly shows that aluminium has undoubtedly a much stronger acid character than silicon.[104]

Vernadsky[713] has drawn special attention to the following facts in support of the acid nature of alumina in the aluminosilicates:

(*a*) The conditions in which aluminosilicates are formed both in the laboratory and in Nature are precisely those which are favourable to the production of aluminates. The minerals of the spinel group separate from molten siliceous masses at high temperatures. A separation of aluminates from such fused materials can only be explained on the assumption that the alumina has an acid character in such aluminates.

(*b*) The separation of aluminosilicates at high temperatures is accompanied by the formation of aluminates (according to the experiments of Vernadsky and Moroziewicz spinels are formed).

(*c*) At much lower temperatures the action of water or carbonic acid solution not infrequently results in the decomposition of aluminosilicates and the separation of aluminates (*vide* Thugutt) or hydrated alumina, with the formation, in Nature, of bauxite or hydrargillite. All these reactions are opposed to the conception that alumina plays the part of a base in the aluminosilicates.

According to Zulkowski[714] the acid nature of alumina in the aluminosilicates explains a fact which has long been regarded as paradoxical by metallurgists, viz. whilst it is found that one molecule of lime effects the slagging or fusion of one molecule of silica, it is also found that just as much lime is required when the silica is combined with alumina. This is incomprehensible if alumina is regarded as basic, but is readily understood if alumina plays the part of an acid.

It should also be observed that Clarke[715] has repeatedly described aluminosilicates as possessing an acid character, and regards the

tourmalines as derivatives of an acid $H_{14}Al_3B_3Si_6O_{31}$, the water in which may be totally replaced.

Other facts are available for showing that silica when combined with alumina behaves in a different manner chemically from what it does in silicates devoid of alumina, and that the aluminosilicates may rightly be regarded as "complexes" as defined by Ostwald (p. 16). Thus:

(*a*) Hautefeuille[105] observed that tungstic anhydride can displace silicic acid from its salts at 900° whilst with aluminosilicates under similar conditions the displaced material contains both silica and alumina and not silica alone.

(*b*) By the action of the hydrates of aluminosilicates on carbonates at a high temperature, CO_2 is liberated and its place is taken by both alumina and silica.

(*c*) Kaolins and other clays possess acid properties and, according to Gorgeu and Ziemjatschewsky respectively, they can decompose haloid salts (KI, KBr, etc.) at high and moderate temperatures, with the liberation of free haloid (acid) and the formation of salt-like aluminosilicates.

(*d*) In various chemical processes—both in Nature and in the laboratory—substitution-reactions frequently occur in which the aluminosilicic radicle remains quite unaffected. All such reactions may be expressed by the following equation:

$$MX + M_1A = M_1X + MA,$$

in which X is the anhydride of an acid, M and M_1, two different metals, and A is the aluminosilicic radicle.

The authors who have maintained the acid character of aluminium in the aluminosilicates and who have recognised the existence of complex aluminosilicic acid in some aluminosilicates have already been mentioned in the historical section of this volume. One of these—Zulkowski—states: "I have . . . also shown that alumina possesses the previously anticipated characteristic of forming compounds which are not salts in the ordinary meaning of this word, but which must be regarded as aluminosilicic acids, and that these acids must occur in certain aluminous slags and glazes."

There are, however, some objections to the hypotheses under discussion:

(*a*) Although in most chemical reactions, the aluminosilicates behave in accordance with the sixth hypothesis, there are others which are, at present, inexplicable or are in direct contradiction to it, as the following examples will show:

1. If the aluminosilicate known as andesite[106],

$$CaO \cdot Na_2O \cdot 2\,Al_2O_3 \cdot 8\,SiO_2,$$

is regarded as a salt of an aluminosilicic acid,

$$2\,H_2O \cdot 2\,Al_2O_3 \cdot 8\,SiO_2,$$

it is easy to understand the formation of analcime from andesite by treatment with Na_2CO_3, which, according to Lemberg, produces the compound

$$2\,Na_2O \cdot 2\,Al_2O_3 \cdot 8\,SiO_2 \text{ (Analcime)}.$$

It is, however, difficult to see why the same chemist could not reproduce andesite from analcime by means of $CaCl_2$. The chief product in the latter case appears to be

$$2\,CaO \cdot 2\,Al_2O_3 \cdot 8\,SiO_2.$$

2. By investigating the behaviour of the compound

$$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2 \text{ (Nepheline)}$$

towards gaseous hydrochloric acid and silver salts, P. Silber[107] has shown that only one-third of the sodium is given up to gaseous hydrochloric acid or is replaceable by silver, the remainder of the sodium being quite unaffected. Yet if the formula of the complex aluminosilicic acid is

$$H_2O \cdot Al_2O_3 \cdot 2\,SiO_2,$$

the sodium atoms, having replaced the whole of the hydrogen, must behave uniformly!

3. If the sixth hypothesis—that the whole of the aluminium is in the form of an acid—is accepted, it follows that all the aluminium atoms must behave similarly to chemical agents. St. J. Thugutt[108] has, however, experimentally proved the exact opposite in a series of aluminosilicates, and has found that one-third of the aluminium behaves differently from the remainder. For example, sodium nepheline hydrate,

$$4\,(Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2) \cdot 5\,H_2O,$$

on prolonged digestion at 200° with 2 per cent. potassium carbonate solution, one-third of the alumina passes into solution in the form of sodium aluminate and a residue of potassium natrolite,

$$K_2O \cdot Al_2O_3 \cdot 3\,SiO_2\,aq.,$$

remains, according to the following equation:

$$3\,(4\,Na_2Al_2Si_2O_8 \cdot 5\,H_2O) + 8\,K_2CO_3 + 9\,H_2O$$
$$= 8\,Na_2CO_3 + 8\,(K_2Al_2Si_3O_{10} + 3\,H_2O) + 4\,Na_2Al_2O_4.$$

Thugutt has also experimentally proved this property of aluminium in the kaolins, and in a series of sodalites or sodium nepheline hydrates in which a portion of the "water of crystallisation" is replaced by several salts such as NaCl, Na_2SO_4, Na_2CO_3, etc.

(*b*) The precise meaning of the term "complex acids" is by no means perfectly clear. As has been shown in the previous pages, all existing theories concerning the constitution of these compounds are only applicable to a comparatively small number of these substances and are not, in other ways, quite free from objection. Hence, the hypothesis that the aluminosilicates are complex acids and salts gives but little information concerning their "constitution" in the true meaning of this word.

(*c*) A theory is only of value if, by its means, a large number of

facts can be arranged systematically. As there can be no doubt, in the present state of our knowledge of the chemical nature of the aluminosilicates, that a genetic relationship exists between the compounds in this group—this being in agreement with the sixth hypothesis—a general systematic arrangement in the sense of the sixth hypothesis must be possible, e.g. one based on the composition of the complex anhydrides. If, however, an attempt is made to apply this arrangement to all the aluminosilicates—including the felspars, micas, clintonites, scapolites, orthochlorites, etc.—a very large number of hypothetical anhydrides is involved; many of these are of a complex composition and their existence has not, so far, been proved.

Vernadśky[109] has actually drawn up a scheme of classification based on chemical properties, but he only applied it to a relatively small number of compounds and made no attempt to arrange the micas, felspars, clintonites and other aluminosilicates in a similar manner, as he realised the impossibility of a complete classification on such a basis.

Hence, although the sixth hypothesis agrees the best with the facts of all the theories mentioned, there are several objections to it, and these must not be under-estimated.

Consequences which follow from the previous Theories

A number of facts may now be mentioned which have a characteristic relation to the theories concerning the aluminosilicates and may be regarded as "consequences" of them.

A. The idea that the constitution of the aluminosilicates cannot be expressed in the light of the previous theories has often led the various investigators to formulate different theories in which no attention was paid to the chemical properties of the aluminates. Amongst these are the so-called "mixture theories" of micas,[110] scapolites,[111] tourmalines,[112] etc. The various investigators differ greatly in what they consider to be the components of the mixtures; these are, in most cases, only hypothetical and are often of such widely different chemical composition that they can scarcely be described as isomorphous in the strict meaning of this term. It is, therefore, impossible to state the constituents of a "mixture" without knowing precisely what a given investigator means by the terms he uses for such constituents.

In this connection it is interesting to note that Clarke[113] has recently suggested that the orthosilicates can form "isomorphous" mixtures with tri-silicates and other poly-silicates. The acceptance of this led Clarke to formulæ which appear to be very improbable. For instance, he suggests for Zinnwaldite[114] the following formulæ :*

1. $Al_{244}Fl_{167}K_{224}Si_{224}H_{116}(AlFl_2)_{20}(Si_3O_8)_{156}(SiO_4)_{306}$,
2. $Al_{239}Fl_{186}Si_{218}H_{112}(AlFl_2)_{209}(Si_3O_8)_{151}(SiO_4)_{312}$.

* Zinnwaldite is usually considered to be an iron-lithium silicate and not a fluorine compound.—A. B. S.

By using the symbol X for both SiO_4 and Si_3O_8 and the symbol R for K, Li, H and AlF_2, he obtained the following constitutional formulæ:

1. $56\,(AlX_3Fl_3R_2) + 53\,(AlX_3R_5) + 45\,(Al_2X_3R_6)$.
2. $62\,(AlX_3Fl_3R_2) + 49\,(AlX_3R_5) + 43\,(Al_2X_3R_3)$.

Re-calculating an analysis of cryophillite[115] made by Riggs, Clarke obtained the following highly complex formula:

$$Al_{[illegible]}Fl_{[illegible]}K_{[illegible]}Li_{[illegible]}H_{[illegible]}(AlFl_2)_{[illegible]}(Si_3O_8)_{[illegible]}(SiO_4)_{[illegible]},$$

and expresses this as:

$$31\,(AlX_3Fl_3R_2) + 81\,(AlX_3R_5) + 25\,(AlX_3R_3).$$

Clarke has also obtained similarly complex formulæ for other silicates including stilbite, chabasite, heulandite,[116] etc. and has endeavoured to explain these in an analogous manner.

B. A somewhat large amount of caprice is observed in studying the representations of the constitution of some silicates. Each investigator selects that arrangement which he considers to be the most convenient for his own use and it is, therefore, very difficult for anyone else to accept any particular theory. The current hypotheses respecting the constitutions of the two following aluminosilicates:

(*a*) $K_2O \cdot Al_2O_3 \cdot 2\,SiO_2$ (Phakelite) and
(*b*) $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$ (Orthoclase),

are typical instances.

(*a*) The Constitution of Phakelite

P. Groth[117] regards this compound as a simple, normal salt of orthosilicic acid, viz.:

$$Si \equiv O_3 \equiv Al$$
$$\diagdown OK.$$

C. Rammelsberg[118] represents it molecularly as:

$$K_4SiO_4 \cdot Al_4Si_3O_{12}.$$

S. J. Thugutt[119] also represents it molecularly, but with other components, viz.:

$$2\,K_2Al_2Si_3O_{10} \cdot K_2Al_2O_4.$$

Vernadsky[120] considers it as a salt of an aluminosilicic acid:

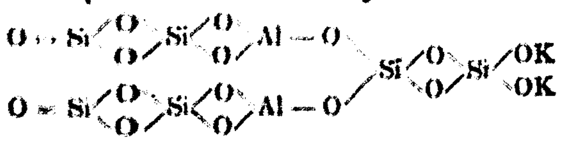
$$H_2O \cdot Al_2O_3 \cdot 2\,SiO_2.$$

(*b*) The Constitution of Potash felspar (orthoclase)

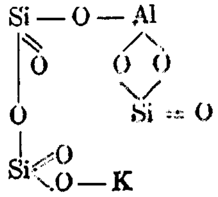
As a product of pseudomorphic processes Tschermak regards orthoclase molecularly as:

$$K_2O \cdot Al_2O_3(SiO_2)_2 \cdot (SiO_2)_4.$$

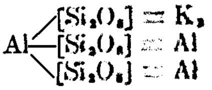
Tschermak[121] represents it atomically:



P. Groth[122] assigns it to the following constitution :



Clarke[123] prefers :



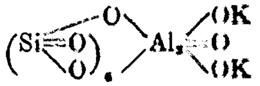
S. J. Thugutt[124], as the result of experiments, uses the following constitutional formula :

$$2\,K_2Al_2Si_3O_{10}\cdot K_2Al_2O_4\cdot 12\,SiO_2.$$

Rammelsberg considers it to be a multiple salt (double salt) analogous to albite and writes the formula :

$$\left\{\begin{matrix} K_2Si_2O_5 + Al_2Si_6O_{15} \\ K_2SiO_3 + Al_2Si_3O_9 \end{matrix}\right\}$$

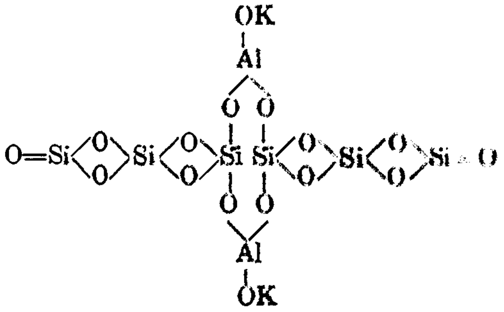
Wartha represents the structural formula of orthoclase as :



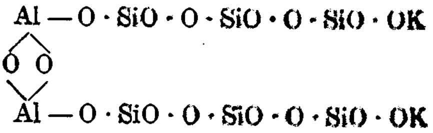
Vernadsky[125] regards orthoclase as a complex salt of an acid :

$$H_2O\cdot Al_2O_3\cdot 6\,SiO_2,$$

and writes its structural formula :

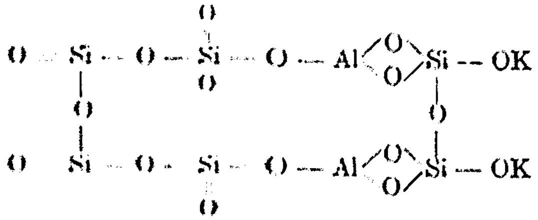


Zulkowski[714] regards felspar as a salt of a complex aluminosilicic acid and gives it the following formula :

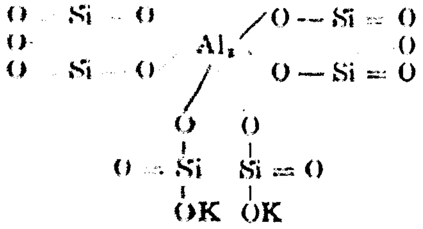


Attention may also be called to the suggestion of Haushofer[716], who, in order to show the genetic relationship of the felspars with granites

and micas, attributed the following constitutional formula to orthoclase:



Mellor and Holdcroft[70a] regard orthoclase as a salt of an aluminohexasilicic acid and suggest the formula:



C. Some aluminosilicates, viewed in the light of existing theories, are extremely puzzling even when they are not highly complex. The formula of ardennite,[126]

$$10\ MnO \cdot V_2O_5 \cdot 5\ Al_2O_3 \cdot 10\ SiO_2 \cdot 5\ H_2O,$$

is thus described by Groth: "This formula—though based on only a few analyses—indicates such a complex structure that it is highly probable that further investigation will lead to its simplification."

This declaration was made by Groth because he was not in a position to find a simpler formula which would agree with the theories mentioned.

D. Another consequence of the current theories is that in many experimental researches no analyses are calculated into formulæ, the usual view being that the substances are not true compounds, but "isomorphous mixtures." It is clear that many interesting characteristics are overlooked in the absence of formulæ. Lemberg[127] is typical of many other investigators who do not express their results by means of formulæ.

The Result of the Critical Examination and the Possibility that the Objections raised to the Sixth Hypothesis are unreal

A critical examination (pp. 8–26) has shown that the aluminosilicates and such complex compounds as the silicotungstates, the phosphotungstates, etc. are closely related substances; it has shown, moreover that, in all probability, both these groups of compounds may be regarded as members of a single class.

With regard to their constitution, this examination only shows that

the structure of every compound is not yet known. The previous theories on the constitution of the aluminosilicates cannot be regarded as satisfactory, as notable objections can be raised against each, and none of them is capable of logical application to the interpretation of the chemical nature of the aluminosilicates as a whole, nor can any of them be used for a systematic classification. At the same time, it should be noted that the conception of the aluminosilicates as complex acids or salts agrees well with the facts.

So long as no better theories are available the sixth hypothesis must claim precedence, in spite of the objections to it already indicated.

It is, however, not improbable that these objections are only *apparent* and that they would be completely overcome if the manner in which the atoms in the anhydrides of the aluminosilicates are bound to each other were known. By the use of a suitable hypothesis for the structure of these anhydrides, a confirmation of this statement may be found. The authors of this present volume have actually formulated such a hypothesis, and its nature and the conclusions which may be drawn from it form the subject-matter of the following pages.*

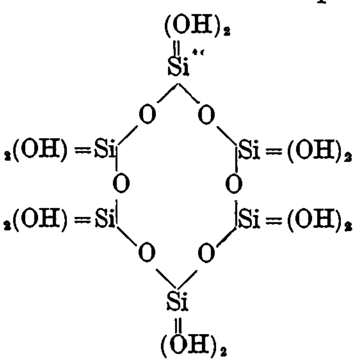
Section III

A Hypothesis to show the Bonding of the Atoms in the Aluminosilicates and related Chemical Compounds

A. Two New Radicals—Hexite and Pentite

1. Hexite

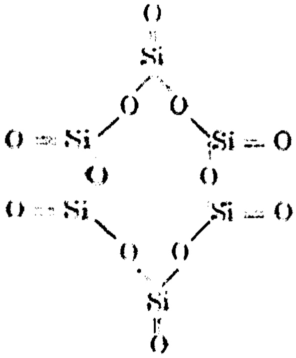
IF six molecules of $Si(OH)_4$ unite together, splitting off water and retaining the quadrivalency of the silicon so as to form a "closed ring," the following constitutional formula is produced :



Formula I.

* In sections I and II the authors have followed Vernadsky : " Über die Gruppe des Sillimanits und die Rolle der Tonerde in den Silicaten " (*Bull. der Moskauer Gesellschaft der Naturforscher*, 1891, 1, 1-100).

If six molecules of water are split off from formula I, the constitution shown in formula II is produced :

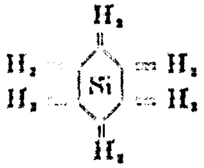


Formula II.

Formula I is shown in abbreviated form by means of the following symbols :

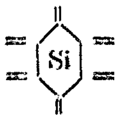
Formula III.

or



Formula IV.

or



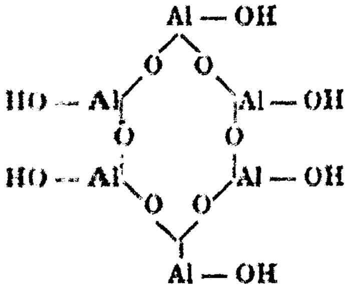
Formula V.

And formula II by the symbol :

Formula VI.

In the following pages these abbreviated forms will be used in place of formulæ I and II.

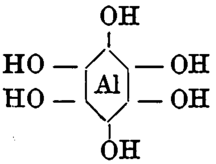
If six molecules $Al(OH)_3$ unite together to form a "ring" after losing six molecules H_2O, but retaining the trivalency of the aluminium, formula VII is obtained :



Formula VII.

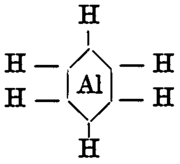
By the removal of three molecules of H_2O from formula VII the anhydride $3\,Al_2O_3$ is produced.

Instead of formula VII, the symbols



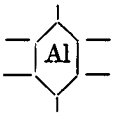
Formula VIII.

or



Formula IX.

or



Formula X.

may be used, the atomic complex $3\,Al_2O_3$ being then represented by

Formula XI.

The radicals indicated by the symbols in formulæ VI and XI are termed "Hexite," $6\,SiO_2$ being known as "Silicon hexite" and $3\,Al_2O_3$ as "Aluminium hexite."

For Silicon hexite and Aluminium hexite the respective symbols

$\hat{Si}$ and $\hat{Al}$

will also be employed.

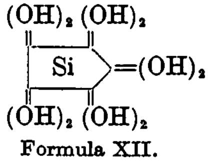
The hydrates of these hexites—such as :

$$6\,H_2O \cdot 6\,SiO_2,$$
$$4\,H_2O \cdot 6\,SiO_2,$$
$$3\,H_2O \cdot 3\,Al_2O_3, \text{ etc.,}$$

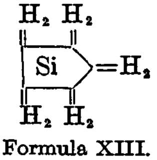
are termed "Hydrohexites."

II. Pentite

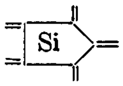
If five molecules of $Si(OH)_4$ or $Al(OH)_3$ form "rings" in a manner similar to hexite, the following structural formulæ are produced :



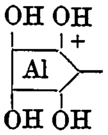
Formula XII.



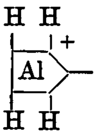
Formula XIII.



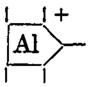
Formula XIV.



Formula XV.



Formula XVI.



Formula XVII.

If the appropriate number of H_2O molecules is removed the anhydrides

Formula XVIII.

Formula XIX.

are obtained.

The meaning of the symbols and formulæ XII–XIX is clear from the statement made with regard to hexite; in addition, the sign + in formulæ XV, XVI, etc. indicates that an even number of these radicles must be present, as such an expression as $\frac{1}{2}$ (5 Al_2O_3) (Formula XIX) is impossible with existing conceptions of molecules.

The ring-forming polymerisation-products represented by formulæ XVIII and XIX are termed "Pentite," that corresponding to $Si(OH)_4$ being referred to as "Silicon pentite," that corresponding to $Al(OH)_3$ as "Aluminium pentite," and the hydrates:

$$5\,H_2O \cdot 5\,SiO_2,$$
$$3\,H_2O \cdot 5\,SiO_2,$$
$$\tfrac{1}{2}\,(5\,H_2O \cdot 5\,Al_2O_3), \text{ etc.,}$$

as "Hydropentites."

The pentites of silicon and aluminium will be indicated by the symbols:

$$\overline{\text{Si}} \text{ and } \overline{\text{Al}},$$

respectively.

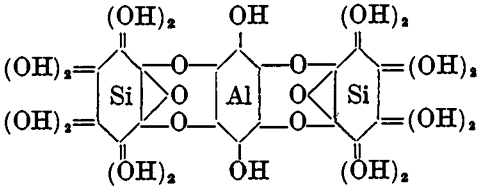
B. The Representation of the Chemical Structure of the Complex Aluminosilicic acids and their Anhydrides by means of the Silicon and Aluminium Pentites and Hexites.

The silicon and aluminium hexites and pentites just mentioned, provide the "building stones" or nuclei for the acids and anhydrides under consideration. With their aid the mode of formation of the acids appears to be in accordance with the following rules:

(*a*) The hydrohexites or hydropentites of aluminium unite with those of silica or *vice versâ*, the two neighbouring hydroxyl groups in the *ortho*-position in these rings splitting off the elements of water, two other OH-groups, also in the ortho-position in the silicon ring, losing their hydrogen atom and forming free H_2O.

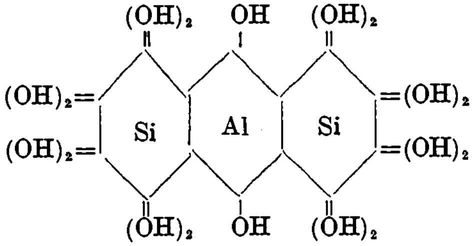
By this means:

1. From one aluminium hydrohexite and two silicon hydrohexites, viz. from $3H_2O \cdot 3Al_2O_3$ and $6H_2O \cdot 6SiO_2$, is obtained the formula:

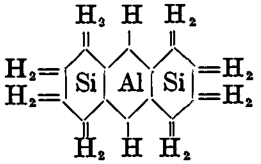


This may be expressed in four abbreviated forms:

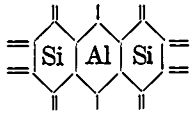
(α)



(β)

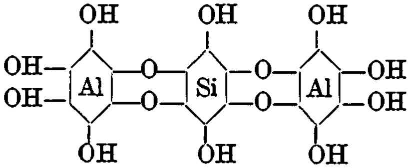


(γ)



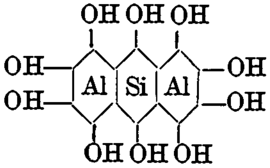
(δ) $H^{\circ}_{18}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$.

2. From a silicon hydrohexite ($3H_2O \cdot 6SiO_2$) and two aluminium hydrohexites ($3H_2O \cdot 3Al_2O_3$) is obtained the formula :

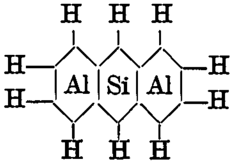


or the symbols :

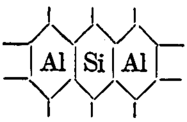
(α)



(β)



(γ)



(δ) $H^{\circ}_{10}(\hat{Al} \cdot \hat{Si} \cdot \hat{Al})$.

3. From one aluminium hydrohexite ($3H_2O \cdot 3Al_2O_3$) and two silicon hydropentites ($5H_2O \cdot 5SiO_2$) are obtained the symbols :

(a)

(b) H°_{2}(Si · Âl · Si),

which need no further explanation.

From (a) it follows that each aluminium hydrohexite can combine with two or at most three silicon hydrohexites or hydropentites, water being split off. The reverse is naturally the case with the silicon hydrohexites ; the hydropentites on the contrary can obviously combine with, at most, two hydrohexites.

(b) Only those types are produced, from the radicles just mentioned, in which the "rings" or nuclei are distributed quite symmetrically. From this it follows :

1. That such types as :

Si · Âl · Ŝi,*
Si · Al · Ŝi,

are completely excluded as they are unsymmetrical.

2. The type

Ŝi · Âl

must be doubled. It then yields two isomeric types :

Ŝi · Âl · Âl · Ŝi,
Âl · Ŝi · Ŝi · Âl, of which

(3) both ends must be formed of absolutely similar radicles, as :

Ŝi · Ál · Ŝi.
Ŝi · Âl · Ŝi · Âl · Ŝi, etc.

It also follows that from the type

Ŝi · Âl · Ŝi

no such isomer as :

Ŝi · Ŝi · Âl

is possible.

(c) The types can only have a group of two similar radicles of the same elements in the middle and not at the ends. Even in the

* If the symbols are doubled and the nuclei symmetrically placed ; such doubled forms are theoretically possible.

middle they cannot have more than two similar radicles of the same substance. The following types are therefore excluded :

$$\hat{Si} \cdot \hat{Si} \cdot \hat{Al} \cdot \dot{Si} \cdot \dot{Si},$$
$$\hat{Si} \cdot \acute{Al} \cdot \hat{Al} \cdot \acute{Al} \cdot \dot{Si},$$
$$\hat{Al} \cdot \hat{Al} \cdot \hat{Si} \cdot \dot{Si} \cdot \hat{Al} \cdot \hat{Al},$$
$$\hat{Al} \cdot \dot{Si} \cdot \dot{Si} \cdot \dot{Si} \cdot \hat{Al}, \text{ etc.}$$

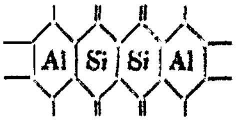
From what has been already stated it will be seen that the following structural formulæ are possible :

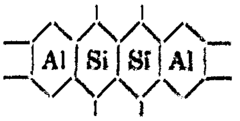
1. $= H^{0}_{20}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) = 10\, H_2O \cdot 6\, Al_2O_3 \cdot 12\, SiO_2,$

2. $= H^{0}_{12}(\hat{Si} \cdot \acute{Al} \cdot \hat{Al} \cdot \hat{Si}) = 6\, H_2O \cdot 6\, Al_2O_3 \cdot 12\, SiO_2,$

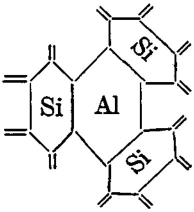
3. $= H^{0}_{16}(\hat{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}) = 8\, H_2O \cdot 6\, Al_2O_3 \cdot 10\, SiO_2,$

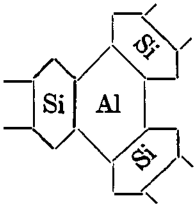
4. $= H^{0}_{10}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \dot{Si}) = 5\, H_2O \cdot 6\, Al_2O_3 \cdot 10\, SiO_2,$

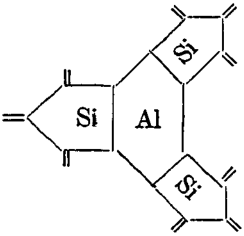
5.  $= H^{0}_{16}(\acute{Al} \cdot \hat{Si} \cdot \dot{Si} \cdot \acute{Al}) = 8\, H_2O \cdot 6\, Al_2O_3 \cdot 12\, SiO_2,$

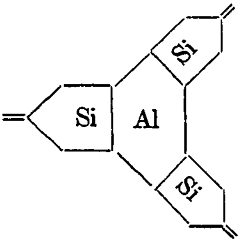
6.  $= H^{0}_{8}(\acute{Al} \cdot \hat{Si} \cdot \acute{Si} \cdot \hat{Al}) = 4\, H_2O \cdot 6\, Al_2O_3 \cdot 12\, SiO_2,$

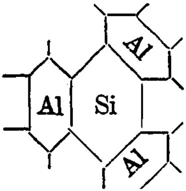
7. $= H^{0}_{12}(Al \cdot \hat{Si} \cdot \hat{Si} \cdot Al) = 6\, H_2O \cdot 5\, Al_2O_3 \cdot 12\, SiO_2,$

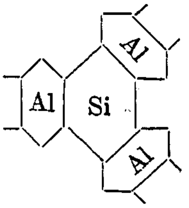
8.  $= H^{o}_{24}\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right) = 12\,H_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$

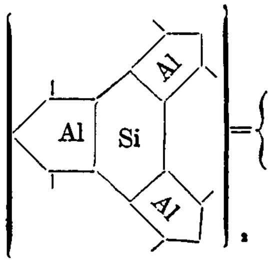
9.  $= H^{o}_{6}\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right) = 3\,H_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$

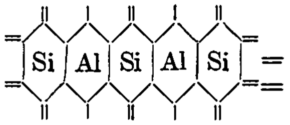
10.  $= H^{o}_{18}\left(\hat{Al}\begin{matrix}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{matrix}\right) = 9\,H_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2$

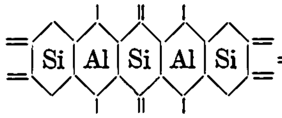
11.  $= H^{o}_{6}\left(\hat{Al}\begin{matrix}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{matrix}\right) = 3\,H_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2$

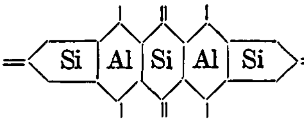
12.  $= H^{o}_{12}\left(\hat{Si}\begin{matrix}\hat{Al}\\ \hat{Al}\\ \hat{Al}\end{matrix}\right) = 6\,H_2O \cdot 6\,SiO_2 \cdot 9\,Al_2O_3$

13.  $= H^{o}_{6}\left(\hat{Si} < \begin{matrix}\hat{Al}\\ \hat{Al}\\ \hat{Al}\end{matrix}\right) = 3\,H_2O \cdot 6\,SiO_2 \cdot 9\,Al_2O_3$

14.  $= \left\{H^{o}_{6}\left(\hat{Si} < \begin{matrix}\overline{Al}\\ \overline{Al}\\ \overline{Al}\end{matrix}\right)\right\}_2 = 6\,H_2O \cdot 12 SiO_2 \cdot 15\,Al_2O_3$

15.  $= H^{o}_{24}\,(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si})$
$= 12\,H_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2$

16.  $= H^{o}_{16}\,(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) = 8\,H_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2$

17.  $= H^{o}_{12}\,(\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{Si}) = 6\,H_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$

etc. etc.

The types produced exclusively from the hexites (e.g. 15 and 16) are termed "primary" or "major types"; those which contain both hexites and "penta radicles" (3, 4, 7, 10, etc.) are known as "secondary" or "minor types."

Having now shown the chief features of the hypothesis relating to the bonding of the atoms in the aluminosilicic acids, it is necessary to ascertain how far the facts support this new theory.

C. Consequences which follow from the "Hexite-Pentite Theory"

I

If the aluminosilicates are really free acids or salts, of which the anhydrides can be produced from aluminium and silicon hexites and pentites in accordance with certain laws or rules, it follows that in that class of reactions known as "double decomposition" the aluminium cannot be replaced by other elements, but that the alumina-silica ratio must remain constant.

Hence in reactions of this kind, involving the following silicates :

$$(a)\ 6\,Na_2O\cdot 6\,Al_2O_3\cdot 12\,SiO_2 = \mathring{Na}_{12}(\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si}),$$
$$(b)\ 3\,Na_2O\cdot 3\,Al_2O_3\cdot 12\,SiO_2 = \mathring{Na}_{6}(\hat{Si}\cdot\hat{Al}\cdot\hat{Si}),$$
$$(c)\ 3\,Na_2O\cdot 3\,Al_2O_3\cdot 10\,SiO_2 = \mathring{Na}_{6}(\overline{Si}\cdot\hat{Al}\cdot\overline{Si}),$$

only those atoms which are outside the brackets (i.e. the sodium atoms) can be replaced by potassium, magnesium, calcium, etc. No such replacement can occur with the aluminium atoms and the alumina-silica ratio must remain unchanged.

As a matter of fact, no replacement of the aluminium by elements which form oxides of the R_2O or RO type has yet been observed either in the so-called pseudomorphous processes or during the course of experimental researches in the laboratory.

Lemberg (see *Appendix*, page following Table IV) by treating an artificially prepared compound

$$0.5\,Na_2O\cdot 5\,K_2O\cdot 6\,Al_2O_3\cdot 16\,SiO_2 = \mathring{Na}\mathring{K}_{10}(\overline{Si}\cdot\hat{Al}\cdot\hat{Si}\cdot\hat{Al}\cdot\overline{Si})$$

with varying amounts of salt-mixtures (sodium and potassium chlorides, potassium and magnesium chlorides, etc.) obtained the following compounds, all having the general formula :

$$\mathring{R}_{11}(\overline{Si}\cdot\hat{Al}\cdot\hat{Si}\cdot\hat{Al}\cdot\overline{Si}),$$

1.	$Na_2O\ \cdot$	$4.5\,K_2O$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
2.	$2\,Na_2O\ \cdot$	$3.5\,K_2O$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
3.	$2.5\,Na_2O\ \cdot$	$3\,K_2O$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
4.	$3\,Na_2O\ \cdot$	$2.5\,K_2O$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
5.	$3.5\,Na_2O\ \cdot$	$2\,K_2O$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
6.	$5\,Na_2O\ \cdot$	$0.5\,K_2O$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
7.	$1.5\,K_2O\ \cdot$	$4\,MgO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
8.	$2\,K_2O\ \cdot$	$3.5\,MgO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
9.	$2.5\,K_2O\ \cdot$	$3\,MgO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
10.	$3\,K_2O\ \cdot$	$2.5\,MgO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
11.	$1.5\,K_2O\ \cdot$	$4\,CaO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
12.	$2\,K_2O\ \cdot$	$3.5\,CaO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$,
13.	$2.25\,K_2O$	$\cdot\,3.25\,CaO$	$\cdot\,6\,Al_2O_3$	$\cdot\,16\,SiO_2$.

From all these thirteen compounds he could only obtain a replacement of the atoms outside the brackets :

$$\mathring{Na}\mathring{K}_{10}(\overline{Si}\cdot\hat{Al}\cdot\hat{Si}\cdot\hat{Al}\cdot\overline{Si}),$$

and the alumina-silica ratio remained constant.

A large number of analogous phenomena might be mentioned, but as they all lead to the same conclusion, the following will suffice. Thus, the silicate

$$(0.5\,Na_2O\cdot 2.5\,CaO\cdot 3\,Al_2O_3\cdot 18\,SiO_2\cdot 17\,H_2O)_2$$

$$= \left\{\mathring{Na}\mathring{Ca}_{2.5}\left(\hat{Al}\begin{matrix}\diagup\hat{Si}\\ -\hat{Si}\\ \diagdown\hat{Si}\end{matrix}\right)\cdot 17\,H_2O\right\}_2$$

is converted by a six weeks' treatment at 100° with KCl (see *Appendix*, Table I, No. 39a) into the compound

$$K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 13\,H_2O = \dot{K}_2\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right) \cdot 13\,H_2O.$$

This potassium salt is converted by a fortnight's treatment at 100° with sodium chloride solution into the sodium salt (see *Appendix*, Table I, No. 39b)

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 16\,H_2O = \dot{Na}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right) \cdot 16\,H_2O.$$

The potassium salt

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot H_2O = \dot{K}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right) \cdot H_2O$$

after a week's treatment at 100° with sodium chloride solution is converted into the sodium salt (see *Appendix*, Table I, No. 39f)

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 8\,H_2O = \dot{Na}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right) \cdot 8\,H_2O.$$

The sodium salt (see *Appendix*, Lemberg's Expts., Series B (c))

$$(3\,Na_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2 \cdot 7\tfrac{1}{2}\,H_2O)_2 = \left\{\dot{Na}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right) \cdot 7.5\,H_2O\right\},$$

is converted after a hundred days' treatment with potassium chloride solution at 200° into the potassium salt

$$(3\,K_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2 \cdot 1\tfrac{1}{2}\,H_2O)_2 = \left\{\dot{K}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right) \cdot 1\tfrac{1}{2}\,H_2O\right\},$$

and the sodium salt

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \dot{Na}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\,H_2O$$

by a three weeks' treatment at 100° with potassium chloride solution (see *Appendix*, Table II, No. 45a) into the potassium salt

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot H_2O = \dot{K}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}) \cdot H_2O,$$

etc., etc.

II

The new hypothesis implies a genetic relationship between the various aluminosilicates; under suitable conditions they must be mutually convertible.

Thus the silicate

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}),$$

can change into the silicates

$$(a)\quad 3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}),$$
$$(b)\quad 3\,MgO \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Mg}_3(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}),\text{ and}$$
$$(c)\quad 3\,CaO \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Ca}_3(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}),$$

the sodium being replaced by potassium, magnesium or calcium.

A conversion of the substance

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}),$$

into the compounds

$$(a)\quad 3\,Na_2O \cdot 3\,Al_2O_3 \cdot 10\,SiO_2 = \overset{\circ}{Na}_6(\bar{Si} \cdot \hat{Al} \cdot \bar{Si}),$$
$$(b)\quad 3\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$
$$(c)\quad 3\,Na_2O \cdot 6\,Al_2O_3 \cdot 10\,SiO_2 = \overset{\circ}{Na}_6(\bar{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \bar{Si}),$$

can be effected, in case (*a*) by the conversion of the silicon hexite into pentite, in (*b*) through the addition of an aluminium hexite and in (*c*) by the simultaneous transformation of the silicon hexite in (*b*) into the corresponding pentite.

In this manner a series of changes in aluminosilicates prepared artificially by Lemberg, Thugutt and others, and the numerous naturally occurring changes which have been observed may be clearly represented.

Thus, Lemberg (see *Appendix*, Series B) :

1. By the action of caustic soda solution of various concentrations on the silicates :

$$(a)\quad 3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O,$$
$$(b)\quad 6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$
$$(c)\quad 6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \overset{\circ}{H}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O,$$

obtained, from the (*a*) compound, the substance

$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 15\,H_2O = \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 15\,H_2O,$$

from (*b*) the substance

$$8\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 7\,H_2O = \overset{\circ}{Na}_{16}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 7\,H_2O,$$

and from (*c*) the silicates

$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 15\,H_2O = \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 15\,H_2O \text{ and}$$
$$8\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 7\,H_2O = \overset{\circ}{Na}_{16}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 7\,H_2O\,;$$

2. By treating the silicates (see *Appendix*, Lemberg Series B).

$$(a)\quad 6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot Si),$$
$$(b)\quad 3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O,\text{ and}$$
$$(c)\quad 3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 = \overset{\circ}{K}_6\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right)$$

with sodium silicate, he obtained from (*a*) and (*b*) the substance

$$(3\,\mathrm{Na_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 15\,\mathrm{SiO_2} \cdot 7\tfrac{1}{2}\,\mathrm{H_2O})_2 = \left\{\mathring{\mathrm{Na}}_6\left(\hat{\mathrm{Al}}\begin{matrix}\bar{\mathrm{Si}}\\ \bar{\mathrm{Si}}\\ \bar{\mathrm{Si}}\end{matrix}\right)\right\}_2 \cdot 15\,\mathrm{H_2O},$$

and from (*c*) the compound

$$3\,\mathrm{Na_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} \cdot 6\,\mathrm{H_2O} = \mathring{\mathrm{Na}}_6(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}) \cdot 6\,\mathrm{H_2O};$$

3. From the silicate

$$(0.5\,\mathrm{Na_2O} \cdot 2.5\,\mathrm{CaO} \cdot 3\,\mathrm{Al_2O_3} \cdot 18\,\mathrm{SiO_2} \cdot 20\,\mathrm{H_2O})_2 = \left\{\mathring{\mathrm{Na}}\mathrm{Ca}_{2.5}\left(\hat{\mathrm{Al}}\begin{matrix}\hat{\mathrm{Si}}\\ \hat{\mathrm{Si}}\\ \hat{\mathrm{Si}}\end{matrix}\right)\right\}_2$$

by treatment for fifteen months at 100° with 20 per cent. sodium carbonate solution he obtained the compound (see *Appendix*, Table II, No. 44)

$$(3\,\mathrm{Na_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 15\,\mathrm{SiO_2} \cdot 7\tfrac{1}{2}\,\mathrm{H_2O})_2 = \left\{\mathring{\mathrm{Na}}_6\left(\hat{\mathrm{Al}}\begin{matrix}\bar{\mathrm{Si}}\\ \bar{\mathrm{Si}}\\ \bar{\mathrm{Si}}\end{matrix}\right)\right\}_2 \cdot 15\,\mathrm{H_2O},$$

and by treatment for two months at 100° with a 25 per cent. solution of sodium silicate, the substance

$$3\,\mathrm{Na_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} \cdot 6\,\mathrm{H_2O} = \mathring{\mathrm{Na}}_6(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}) \cdot 6\,\mathrm{H_2O};$$

4. From the silicates:

$$6\,\mathrm{H_2O} \cdot 6\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} \cdot 6\,\mathrm{H_2O} = \mathring{\mathrm{H}}_{12}(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}) \cdot 6\,\mathrm{H_2O},$$

$$6\,\mathrm{Na_2O} \cdot 6\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} = \mathring{\mathrm{Na}}_{12}(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}),$$

$$6\,\mathrm{Na_2O} \cdot 6\,\mathrm{Al_2O_3} \cdot 18\,\mathrm{SiO_2} \cdot 12\,\mathrm{H_2O} = \mathring{\mathrm{Na}}_{12}(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}) \cdot 12\,\mathrm{H_2O},$$

$$3\,\mathrm{Na_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} \cdot 6\,\mathrm{H_2O} = \mathring{\mathrm{Na}}_6(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}) \cdot 6\,\mathrm{H_2O},$$

$$3\,\mathrm{K_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} = \mathring{\mathrm{K}}_6(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}), \text{ and}$$

$$3\,\mathrm{K_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 18\,\mathrm{SiO_2} = \mathring{\mathrm{K}}_6\left(\hat{\mathrm{Al}}\begin{matrix}\hat{\mathrm{Si}}\\ \hat{\mathrm{Si}}\\ \hat{\mathrm{Si}}\end{matrix}\right)$$

by treatment with a mixture of sodium chloride and caustic soda (see *Appendix*, Lemberg Series A) he obtained a "sodalite":

$$(6\,\mathrm{Na_2O} \cdot 6\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2}) \cdot 4\,\mathrm{NaCl} \cdot 4\,\mathrm{H_2O}$$
$$= \mathring{\mathrm{Na}}_{12}(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}) \cdot 4\,\mathrm{NaCl} \cdot 4\,\mathrm{H_2O};$$

5. From

$$3\,\mathrm{K_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 12\,\mathrm{SiO_2} = \mathring{\mathrm{K}}_6(\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}), \text{ and}$$

$$3\,\mathrm{K_2O} \cdot 3\,\mathrm{Al_2O_3} \cdot 18\,\mathrm{SiO_2} = \mathring{\mathrm{K}}_6\left(\hat{\mathrm{Al}}\begin{matrix}\hat{\mathrm{Si}}\\ \hat{\mathrm{Si}}\\ \hat{\mathrm{Si}}\end{matrix}\right)$$

he obtained the "sodalite"

$$(6\ K_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ KCl \cdot 8\ H_2O$$
$$= K_{12}(Si \cdot \dot{Al} \cdot \dot{Al} \cdot Si) \cdot 2\ KCl \cdot 8\ H_2O,$$

by treatment with a mixture of potassium chloride and caustic potash.

6. From the silicates:

$$6\ H_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \dot{H}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\ H_2O,$$
$$6\ Na_2O \cdot 6\ Al_2O_3 \cdot 18\ SiO_2 \cdot 12\ H_2O = Na_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Si} \cdot \dot{Al} \cdot \dot{Si}) \cdot 12\ H_2O,$$
$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \dot{Na}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\ H_2O,$$
$$3\ K_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 = K_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}),$$
$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 = \dot{Na}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right)$$
$$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 = K_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right)$$

and a mixture of sodium sulphate and caustic soda he obtained the "sodalite"

$$(6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_2SO_4 \cdot 6\ H_2O$$
$$= \dot{Na}_{12}(Si \cdot \dot{Al} \cdot \dot{Al} \cdot Si) \cdot 2\ Na_2SO_4 \cdot 6\ H_2O;$$

7. From the compounds:

$$6\ H_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \dot{H}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\ H_2O,$$
$$6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 = \dot{Na}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}),$$
$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \dot{Na}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\ H_2O,$$
$$3\ K_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 = \dot{K}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}),$$
$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 = \dot{Na}_6\left(\dot{Al}\begin{matrix}\dot{Si}\\ \dot{Si}\\ \dot{Si}\end{matrix}\right)$$

and sodium silicate he obtained the "sodalite"

$$(6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_2SiO_3 \cdot 8\ H_2O$$
$$= \dot{Na}_{12}(Si \cdot \dot{Al} \cdot \dot{Al} \cdot Si) \cdot 2\ Na_2SiO_3 \cdot 8\ H_2O;$$

8. From the silicates:

$$6\ H_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \dot{H}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\ H_2O,$$
$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \dot{Na}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\ H_2O,$$
$$3\ K_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 = \dot{K}_6(\dot{Si} \cdot \dot{Al} \cdot \dot{Si}),$$

and a mixture of sodium carbonate and caustic soda he obtained the "sodalite"

$$3\ (6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 4\ Na_2CO_3 \cdot 30\ H_2O$$
$$= \{\dot{Na}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si})\}_3 \cdot 4\ Na_2CO_3 \cdot 30\ H_2O.$$

From these researches of Lemberg's a genetic relationship between the compounds of the five following types:

1. $\dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}}$.
2. $\dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}}$.
3. $\dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}}$.
4. and
5.

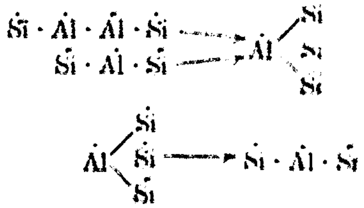
can be traced. This is shown in the following Table:

Table showing the Results of Lemberg's Researches

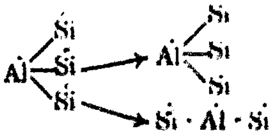
(*a*) Series 1.

$$\dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}} \longrightarrow \dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}}.$$

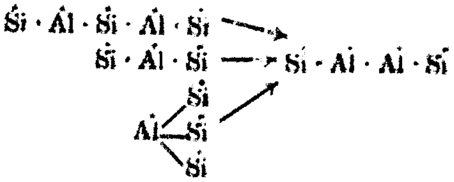
(*b*) Series 2.



(*c*) Series 3.



(*d*) Series 4, 5, 6, 7 and 8.



The experimental researches of Thugutt produce analogous results: By digesting kaolin[139]

(*a*) $6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \dot{H}_{12}(\dot{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Al}} \cdot \dot{\mathrm{Si}}) \cdot 6\,H_2O$.

with 2 per cent. caustic potash solution at 192–202° he obtained a compound

(*b*) $6\,K_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 18\,H_2O = \overset{\circ}{K}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 18\,H_2O$;

with 1 per cent. caustic soda solution, a compound

(*c*) $6\,Na_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 \cdot 10\,H_2O = \overset{\circ}{Na}_{12}(\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{\overline{Si}}) \cdot 10\,H_2O$;

with a mixture of caustic potash and potassium silicate two products

(*d*) $$3\,H_2O \cdot 6\,K_2O \cdot 6\,Al_2O_3 \cdot 15\,SiO_2 \cdot 6\,H_2O$$
$$= \overset{\circ}{H}_6\overset{\circ}{K}_{12}(\overline{Si} \cdot \hat{Al} \cdot \overline{\overline{Si}} \cdot \hat{Al} \cdot \overline{Si}) \cdot 6\,H_2O,$$

(*e*) $3\,K_2O \cdot 3\,Al_2O_3 \cdot 10\,SiO_2 \cdot aq. = \overset{\circ}{K}_6(\overline{Si} \cdot \hat{Al} \cdot \overline{\overline{Si}})\,aq.$

From the above-mentioned experimental researches of Thugutt a genetic relationship may be shown between the compounds of the types:

(*a*) $\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}$,
(*b*) $\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}$,
(*c*) $\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{Si}$,
(*d*) $\overline{\overline{Si}} \cdot \hat{Al} \cdot \overline{Si} \cdot \hat{Al} \cdot \overline{\overline{Si}}$,
(*e*) $\overline{\overline{Si}} \cdot \hat{Al} \cdot \overline{\overline{Si}}$.

From these results it follows that compounds of type (*a*) may be converted into those of type (*b*), (*c*), (*d*), and (*e*).

Friedel has, however, found that compounds such as

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}$$

can also be converted into those of other types. By treating muscovite:

$$4\,H_2O \cdot 2\,K_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{H}_8\overset{\circ}{K}_4(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

with a mixture of potassium silicate and potassium carbonate, Friedel[140] obtained the compound

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 = \overset{\circ}{K}_6\left(\hat{Al}\begin{array}{l}\diagup \hat{Si}\\ - \hat{Si}\\ \diagdown \hat{Si}\end{array}\right)$$

Interesting conversions of aluminosilicates have also been observed in Nature (pseudomorphous processes); these give results analogous to the experimental researches just mentioned.

Analcime[141]

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$$

can change into muscovite

$$4\,H_2O \cdot 2\,K_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \overset{\circ}{H}_8\overset{\circ}{K}_4(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

and prehnite

$$12\,CaO \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 6\,H_2O = \overset{\circ}{Ca}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O.$$

The silicates:

$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$ (nepheline) $= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$,
$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (leucite) $= \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$,
$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 4\,NaCl$ (sodalite) $= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 4\,NaCl$,
$3\,CaO \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 12\,H_2O$ (laumontite) $= \mathring{Ca}_3(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 12\,H_2O$

may all change into analcime[142]

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}).$$

In Nature, orthoclase[143]

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 = \mathring{K}_6\left(\hat{Al} \begin{array}{l} \diagup \hat{Si} \\ - \hat{Si} \\ \diagdown \hat{Si} \end{array}\right)$$

has also been found to change into

$6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O$ (kaolin) $= \mathring{H}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O$
$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (analcime) $= \mathring{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$
$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 12\,H_2O$ (natrolite) $= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 12\,H_2O$
$2\,H_2O \cdot 8\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$ (epidote) $= \mathring{H}_4\mathring{Ca}_8(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
$3\,H_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (pyrophillite) $= \mathring{H}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$
$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$ (albite) $= \mathring{Na}_6\left(\hat{Al} \begin{array}{l} \diagup \hat{Si} \\ - \hat{Si} \\ \diagdown \hat{Si} \end{array}\right)$
$4\,H_2O \cdot 2\,K_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$ (muscovite) $= \mathring{H}_8\mathring{K}_4(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$.

Natural orthoclase[144] is formed from

$3\,CaO \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (laumontite) $= \mathring{Ca}_3(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$,
$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (analcime) $= \mathring{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$,
$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (leucite) $= \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$, and
$12\,CaO \cdot 6\,Al_2O_3 \cdot 18\,SiO_2$ (prehnite) $= \mathring{Ca}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si})$.

Leucite[145]

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}),$$

may be changed into nepheline:

$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

and nepheline into natrolite:

$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 12\,H_2O = \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot Si)\,12\,H_2O,$$

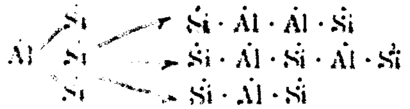
etc., etc.

Table showing the Natural Changes of the Aluminosilicates

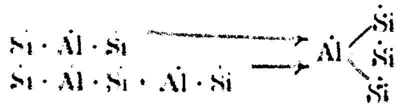
1. $\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \begin{array}{l} \longrightarrow \hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si} \\ \longrightarrow \hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si} \end{array}$

2. $\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si} \begin{array}{l} \longrightarrow \hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si} \\ \longrightarrow \hat{Si} \cdot \hat{Al} \cdot \hat{Si} \end{array}$

3.



4.



In consequence of the great variety of silicates, the various products formed from them by the action of the weather are naturally very numerous. The members of the felspar group are particularly distinguished by the multiplicity of their products. For instance, potash felspar is converted, on weathering, into kaolin, whilst other weather-products (in the formation of which water as well as air is necessary) are muscovite and epidote, with, less frequently, chlorite and zeolite. Lime felspar, on weathering, forms calcareous zeolite (chabasite, phillipsite, desmine, heulandite, and, less frequently, laumontite, skolezite, etc.). Soda felspar forms sodic zeolites (analcime, natrolite, etc.).

The scapolite minerals, on active weathering, produce epidote, albite, biotite or muscovite and, finally, kaolin.

The tourmalines are seldom affected by the weather, but if so they produce mica, chlorite, etc.

Some zeolites (analcime, laumontite, prehnite) are converted into felspars on exposure to the weather. The zeolites may also be converted into other zeolites, as natrolite into prehnite, analcime into natrolite, and chabasite into natrolite.

The researches of Lemberg, Thugutt, and Doelter have shown that zeolites are easily converted into other compounds by addition to, subtraction from, or replacement of, some of their constituents.

Vernadsky[213] has observed that when granite is fused, aluminosilicates (e.g. anorthite) and orthosilicates (e.g. olivine) are produced, as in the researches of Doelter and others. The granites may also be formed by a reverse reaction from orthosilicates and aluminosilicates at a high temperature. Granites are also converted into mica, chlorite, minerals of the nepheline group, clays, etc.

All these changes are in accordance with the second consequence of the new hypothesis, and the existence of a genetic relationship between the various aluminosilicates may now be regarded as a fact which is established beyond dispute. The nature of this relationship can also be satisfactorily explained by the proposed theory.

III

The hexite-pentite hypothesis renders possible a system of complete chemical classification of the aluminosilicates on the basis of their nature as complex anhydrides.

In order to see how far the consequences of accepting this theory agree with the facts, it was decided to calculate the formulæ of a large number of the analyses of aluminosilicates published in Hintze's "Handbuch."

As some atoms or atomic groups can be replaced by analogous ones —e.g. the atoms K, Na, Li or Ca, Mg, Fe'', or the atomic groups Al_2O_3, Fe_2O_3, Cr_2O_3, Mn_2O_3, etc., or SiO_2, TiO_2, etc., it was considered desirable to make the calculation of the formulæ in such a manner that, instead of calculating the number of atoms of each substance separately, the replaceable substances were taken together in groups, thus :

$Si_6Al_2(Ca, Na_2, K_2)O_{16} \cdot 6\,H_2O$ (desmine).[146]
$(Si_2O_5)_2Al(Li, Na, H)$ (petalite).[147]
$(Si, Ti)_4O_{12}(Fe, Mn)(Na, K)_2$ (neptunite).[148]

This method of simplifying the calculation is due to Berzelius[149], who recommended its use—not for all cases, but for those in which the constituents of a substance bear no simple relation to each other.

Gerhardt[150], who undertook a re-formulation of the silicates, did not follow the suggestion of Berzelius, but added the various bases (such as lime and magnesia) together, even when they bore a simple relation to each other. The authors of the present volume prefer, however, to adopt a grouping which more closely resembles that of Berzelius.

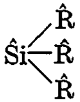
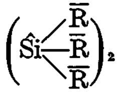
By this means it is possible to convert the true formula,* the interpretation of which is almost impossible on account of the presence of a number of substances in small quantities—into a formula which is simpler, and in many cases—but not all—to produce a formula which may be interpreted with ease.

In re-arranging the formulæ, the authors have endeavoured to keep as near to the true formula as possible, so as to obtain results as quantitative as well as merely qualitative value. In many instances this led to apparently complex formulæ, but even these may be represented atomically.

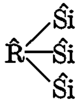
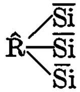
Calculations, by this means, of the formulæ from a large number of analyses of clintonite, mica, scapolite, orthochlorite, tourmaline, and felspar, showed that many compounds of this group may be arranged quite systematically, according to the type to which they belong. The results of this calculation of the formulæ from the analytical figures are given in the *Appendix*. The following types are selected because a large number of the compounds previously mentioned will be found to fit them.

* The conversion of all the analytical figures into molecular ratios is termed the "true formula" as distinct from the approximate formula due to the simplification proposed.

A. Types of the Clintonite Group *

I.	$\hat{R} \cdot \widehat{Si} \cdot \hat{R}$	$= 6\,R_2O_3 \cdot 6\,SiO_2$,
II.	$\overline{R} \cdot \widehat{Si} \cdot \overline{R}$	$= 5\,R_2O_3 \cdot 6\,SiO_2$,
III.	$\widehat{Si} \cdot \hat{R} \cdot \hat{R} \cdot \widehat{Si}$	$= 6\,R_2O_3 \cdot 12\,SiO_2$,
IV.	$\widehat{Si} \cdot \overline{R} \cdot \overline{R} \cdot \widehat{Si}$	$= 5\,R_2O_3 \cdot 12\,SiO_2$,
V.	$\widehat{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \widehat{Si}$	$= 6\,R_2O_3 \cdot 18\,SiO_2$,
VI.	$\overline{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \overline{Si}$	$= 6\,R_2O_3 \cdot 16\,SiO_2$,
VII.	$\hat{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \hat{R}$	$= 9\,R_2O_3 \cdot 12\,SiO_2$,
VIII.	$\overline{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \overline{R}$	$= 8\,R_2O_3 \cdot 12\,SiO_2$,
IX.		$= 9\,R_2O_3 \cdot 6\,SiO_2$,
X.		$= 15\,R_2O_3 \cdot 12\,SiO_2$.

B. Types of the Mica Group

I.	$\widehat{Si} \cdot \hat{R} \cdot \widehat{Si}$	$= 3\,R_2O_3 \cdot 12\,SiO_2$,
II.	$\overline{Si} \cdot \hat{R} \cdot \overline{Si}$	$= 3\,R_2O_3 \cdot 10\,SiO_2$,
III.		$= 3\,R_2O_3 \cdot 18\,SiO_2$,
IV.		$= 3\,R_2O_3 \cdot 15\,SiO_2$,
V.	$\hat{R} \cdot \widehat{Si} \cdot \hat{R}$	$= 6\,R_2O_3 \cdot 6\,SiO_2$,
VI.	$\overline{R} \cdot \widehat{Si} \cdot \overline{R}$	$= 5\,R_2O_3 \cdot 6\,SiO_2$,
VII.	$\widehat{Si} \cdot \hat{R} \cdot \hat{R} \cdot \widehat{Si}$	$= 6\,R_2O_3 \cdot 12\,SiO_2$,
VIII.	$\overline{Si} \cdot \hat{R} \cdot \hat{R} \cdot \overline{Si}$	$= 6\,R_2O_3 \cdot 10\,SiO_2$,
IX.	$\widehat{Si} \cdot \overline{R} \cdot \overline{R} \cdot \widehat{Si}$	$= 5\,R_2O_3 \cdot 12\,SiO_2$,
X.	$\widehat{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \widehat{Si}$	$= 6\,R_2O_3 \cdot 18\,SiO_2$,
XI.	$\overline{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \overline{Si}$	$= 6\,R_2O_3 \cdot 16\,SiO_2$,
XII.	$\widehat{Si} \cdot \overline{R} \cdot \widehat{Si} \cdot \overline{R} \cdot \widehat{Si}$	$= 5\,R_2O_3 \cdot 18\,SiO_2$,
XIII.	$\hat{R} \cdot \widehat{Si} \cdot \hat{R} \cdot \widehat{Si} \cdot \hat{R}$	$= 9\,R_2O_3 \cdot 12\,SiO_2$,
XIV.	$\overline{Si} \cdot \hat{R} \cdot \overline{Si} \cdot \hat{R} \cdot \overline{Si} \cdot \hat{R} \cdot \overline{Si}$	$= 9\,R_2O_3 \cdot 20\,SiO_2$.

* In the *Appendix* the types are arranged in the order of the R_2O_3 present; on the present page they are placed according to their relationship with respect to their chemical structure.

C. Types of the Scapolite Group

I.	$\hat{Si}\cdot\hat{R}\cdot\hat{Si}$	$= 3\,R_2O_2\cdot 12\,SiO_2,$
II.	$\overline{Si}\cdot\hat{R}\cdot\overline{Si}$	$= 3\,R_2O_3\cdot 10\,SiO_2,$
III.	$\hat{Si}\cdot\hat{R}\cdot\hat{R}\cdot\hat{Si}$	$= 6\,R_2O_3\cdot 12\,SiO_2,$
IV.	$\hat{Si}\cdot\overline{R}\cdot\overline{R}\cdot\hat{Si}$	$= 5\,R_2O_3\cdot 12\,SiO_2,$
V.	$\hat{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{R}\cdot\hat{Si}$	$= 6\,R_2O_3\cdot 18\,SiO_2,$
VI.	$\overline{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{R}\cdot\overline{Si}$	$= 6\,R_2O_3\cdot 16\,SiO_2,$
VII.	$\hat{Si}\cdot\overline{R}\cdot\hat{Si}\cdot\overline{R}\cdot\hat{Si}$	$= 5\,R_2O_3\cdot 18\,SiO_2,$
VIII.	$\overline{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{Si}\cdot\hat{R}\cdot\overline{Si}$	$= 6\,R_2O_3\cdot 22\,SiO_2,$
IX.	$\overline{Si}\cdot\overline{R}\cdot\hat{Si}\cdot\hat{Si}\cdot\overline{R}\cdot\overline{Si}$	$= 5\,R_2O_3\cdot 22\,SiO_2,$
X.	$\overline{Si}\cdot\hat{R}\cdot\overline{Si}\cdot\hat{R}\cdot\overline{Si}\cdot\hat{R}\cdot\overline{Si}$	$= 9\,R_2O_3\cdot 20\,SiO_2,$
XI.	$\hat{R}\left\langle\begin{array}{l}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{array}\right.$	$= 3\,R_2O_3\cdot 15\,SiO_2.$

D. Types of the Orthochlorite Group

I.	$\hat{Si}\cdot\hat{R}\cdot\hat{Si}$	$= 3\,R_2O_3\cdot 12\,SiO_2,$
II.	$\overline{Si}\cdot\hat{R}\cdot\overline{Si}$	$= 3\,R_2O_3\cdot 10\,SiO_2,$
III.	$\hat{R}\left\langle\begin{array}{l}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{array}\right.$	$= 3\,R_2O_3\cdot 18\,SiO_2,$
IV.	$\hat{R}\left\langle\begin{array}{l}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{array}\right.$	$= 3\,R_2O_3\cdot 15\,SiO_2,$
V.	$\hat{R}\cdot\hat{Si}\cdot\hat{R}$	$= 6\,R_2O_3\cdot 6\,SiO_2,$
VI.	$\overline{R}\cdot\hat{Si}\cdot\overline{R}$	$= 5\,R_2O_3\cdot 6\,SiO_2,$
VII.	$\hat{Si}\cdot\hat{R}\cdot\hat{R}\cdot\hat{Si}$	$= 6\,R_2O_3\cdot 12\,SiO_2,$
VIII.	$\overline{Si}\cdot\hat{R}\cdot\hat{R}\cdot\overline{Si}$	$= 6\,R_2O_3\cdot 10\,SiO_2,$
IX.	$\hat{Si}\cdot\overline{R}\cdot\overline{R}\cdot\hat{Si}$	$= 5\,R_2O_3\cdot 12\,SiO_2,$
X.	$\hat{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{R}\cdot\hat{Si}$	$= 6\,R_2O_3\cdot 18\,SiO_2,$
XI.	$\hat{Si}\cdot\overline{R}\cdot\hat{Si}\cdot\overline{R}\cdot\hat{Si}$	$= 5\,R_2O_3\cdot 18\,SiO_2,$
XII.	$\overline{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{R}\cdot\overline{Si}$	$= 6\,R_2O_3\cdot 16\,SiO_2,$
XIII.	$\hat{R}\cdot\hat{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{R}$	$= 9\,R_2O_3\cdot 12\,SiO_2,$
XIV.	$\overline{R}\cdot\hat{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\overline{R}$	$= 8\,R_2O_3\cdot 12\,SiO_2,$
XV.	$\overline{Si}\cdot\overline{R}\cdot\hat{Si}\cdot\hat{Si}\cdot\overline{R}\cdot\overline{Si}$	$= 5\,R_2O_3\cdot 22\,SiO_2.$

E. Types of the Tourmaline Group

I.	$\hat{R}\cdot\hat{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\hat{R}$	$= 9\,R_2O_3\cdot 12\,SiO_2,$
II.	$\overline{R}\cdot\hat{Si}\cdot\hat{R}\cdot\hat{Si}\cdot\overline{R}$	$= 8\,R_2O_3\cdot 12\,SiO_2,$
III.	$\overline{R}\cdot\hat{Si}\cdot\overline{R}$	$= 5\,R_2O_3\cdot 6\,SiO_2.$

F. Types of the Felspar Group

I.	$\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 24\,SiO_2$,
II.	$\overline{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \overline{Si} = 6\,R_2O_3 \cdot 22\,SiO_2$,
III.	$\overline{Si} \cdot \hat{R} \cdot \overline{Si} \cdot \overline{Si} \cdot \hat{R} \cdot \overline{Si} = 6\,R_2O_3 \cdot 20\,SiO_2$,
IV.	$\hat{Si} \cdot \overline{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \overline{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 24\,SiO_2$,
V.	$\overline{Si} \cdot \overline{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \overline{R} \cdot \overline{Si} = 5\,R_2O_3 \cdot 22\,SiO_2$.

A large number of aluminosilicates may be arranged according to the authors' system (see *Appendix*). Whether this classification is suitable for all aluminosilicates can only be ascertained by means of more analyses and by calculating more formulæ.

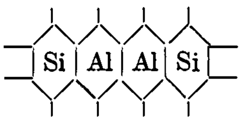
IV

The structural formulæ devised by the authors show that the aluminium and silicon atoms in an aluminosilicate do not always behave the same in chemical and physico-chemical investigations. Under certain circumstances some of these atoms behave differently from the remainder, and the same is true of the monovalent and divalent elements in these compounds.

It not infrequently happens that the hydroxyl groups which form the "water of constitution" in the aluminosilicates are replaced by the halogens: fluorine, and chlorine. The structural formulæ show that, in the latter case, halogen atoms may be united in various ways in a single aluminosilicate and that these atoms must produce different chemical or physico-chemical properties according to their position in the whole molecule. A few examples will make this clearer.

In type I

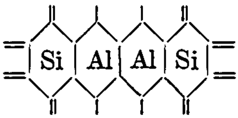
I.



1. $\frac{1}{3}$ of the aluminium,
2. $\frac{1}{3}$ of the silicon,
3. $\frac{1}{3}$ of the base or hydroxyl groups or the substitutes Cl, Fl, etc. must clearly behave differently from the other $\frac{2}{3}$.

In type II

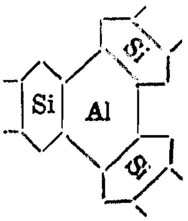
II.



the aluminium and silicon must behave in a manner analogous to those in type I, but $\frac{1}{3}$ of the base (or the hydroxyl groups and their substitutes) behaves differently from the remainder.

In type III

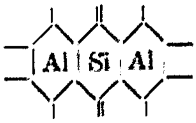
III.



only $\frac{1}{3}$ of the silicon will behave differently from the remainder.

In type IV

IV.



1. $\frac{1}{3}$ of the aluminium,
2. $\frac{1}{3}$ of the silicon,
3. $\frac{1}{3}$ of the base (or the hydroxyl groups or their substitutes)

behave differently from the rest.

In types V and VI

V.

VI.

1. $\frac{1}{3}$ of the aluminium,
2. $\frac{4}{7}$ of the base (Type V), or $\frac{3}{7}$ of it (Type VI) must behave differently from the rest.

Some of these interesting results are fully confirmed by experiments and researches already published.

In compounds of type I, such as kaolin,

$$6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \dot{H}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}) \cdot 6\,H_2O,$$

nepheline hydrate,

$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot aq. = \dot{Na}_{12}(\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si})aq.,$$

and a number of "sodalites," i.e. derivatives of nepheline hydrate (see p. 59), which, according to Thugutt, are so constituted that part of their "water of crystallisation" is replaced by a given salt ($NaCl$, Na_2SO_4, etc.). The author just mentioned reached precisely the same conclusions as the authors of the hexite-pentite theory, viz. that one-third of the aluminium behaves differently from the remainder. Thugutt therefore suggests the following constitutional formulae :

$$2\,H_2Al_2Si_3O_{10} \cdot H_2Al_2O_4 \cdot 3\,H_2O \text{ (kaolin)},$$
$$4\,(2\,Na_2Al_2Si_3O_{10} \cdot Na_2Al_2O_4) \cdot 15\,H_2O \text{ (nepheline)}.$$

P. Silber (p. 25) has shown that the behaviour of the compound :

$$6\,Na_2O\cdot 6\,Al_2O_3\cdot 12\,SiO_2\ \text{(nepheline)} = \overset{\circ}{Na}_{12}(\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si})$$

of the same type towards gaseous hydrochloric acid and silver solutions indicates that $\frac{1}{3}$ of the sodium behaves differently from the remainder, and thus confirms the hexite-pentite theory.

The authors believe that confirmation of the constitution of compounds of type II is to be found in a new set of formulæ for the epidotes (see *Appendix*). The minerals in this group are chiefly compounds of type II with the general formula :

$$2\,H_2O\cdot 8\,CaO\cdot 6\,R_2O_3\cdot 12\,SiO_2 = \overset{\circ}{H}_4\overset{\circ}{Ca}_8(\hat{Si}\cdot\hat{R}\cdot\hat{R}\cdot\hat{Si})$$
$$R = Al,\ Fe.$$

The constancy of the ratio of lime to "water of constitution" in these minerals makes it highly probable that $\frac{1}{6}$ of the hydroxyl groups in the acids corresponding to these minerals behaves differently from the remainder.

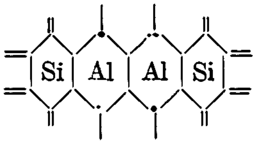
By replacing part of the aluminium by Fe''' in the formula

$$2\,H_2O\cdot 8\,CaO\cdot 6\,Al_2O_3\cdot 12\,SiO_2,$$

the various epidotes are produced and no epidote has yet been found with a higher content than is shown in the formula (see *Appendix*):

$$2\,H_2O\cdot 8\,CaO\cdot 2\,Fe_2O_3\cdot 4\,Al_2O_3\cdot 12\,SiO_2.$$

It appears probable that, under the conditions under which epidotisation can occur in Nature, only those aluminium atoms which are indicated by a dot in the formula below can be replaced by Fe≡



For the prognosis of type III, Thugutt's work on a compound of this type—potash felspar :

$$3\,K_2O\cdot 3\,Al_2O_3\cdot 18\,SiO_2 = \overset{\circ}{K}_8\left(\hat{Al}\begin{cases}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{cases}\right)$$

is important. According to Thugutt, this substance, on treatment with 2 per cent. caustic potash solution, loses silica and forms other compounds which are incapable of exact analysis, but, so far as he has ascertained it, their composition agrees with the theory formulated by the authors, viz. that the constitutional formula of potash felspar (which, according to Thugutt, is $2\ K_2Al_2Si_3O_{10}\cdot K_2Al_2O_4\cdot 12\ SiO_2$) suggests that $\frac{1}{3}$ of the silicon behaves differently from the remainder.

A partial confirmation of the prognosis of type IV appears to be

supplied by the composition of the minerals known by the general name of "topaz." Calculations of the formulæ of these compounds from a number of analyses (see *Appendix*) showed that they belong, in part, to type IV and may be represented by :

1. $Si_6Al_{12}Fl_8O_{26}$,
2. $Si_6Al_{12}Fl_9O_{25 \cdot 5}$,
3. $Si_6Al_{12}Fl_{10}O_{25}$,
4. $Si_6Al_{12}Fl_{11}O_{24 \cdot 5}$,
5. $Si_6Al_{12}Fl_{12}O_{24}$.

These formulæ are based on the assumption that one atom of oxygen may be replaced by two of fluorine.

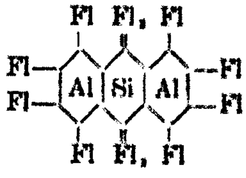
It appears probable that the hydrogen present in these compounds has been overlooked.

If this assumption is admitted—and the presence of hydrogen has been independently proved by (*a*) Jannasch and Locke[123] and (*b*) Penfield and Minor—the topazes are derived from the hydrate :

$Si_6Al_{12}O_{24}(OH)_{12}$

The researches of Penfield and Minor showed that water in a strongly combined state is present in the topazes. In an investigation of topaz from Stoneham, which contained 0·98 per cent. of water, the powder lost only 0·12 per cent. at the highest temperature obtainable by means of a ring-burner (see Penfield and Minor, *Zeitschr. f. Krystallogr. u. Mineral.* 1894, 23, 321). It is thus clear that the water contained in topaz may easily be overlooked. The investigators just quoted have found that the water is liberated quantitatively on fusing a topaz with sodium carbonate. The correctness of the view that topaz contains water in the form of OH-groups is also confirmed by the following interesting characteristics of topaz : the specific gravity, the double refraction, the apparent angle of the optical axes (2 *e*) and the crystallographic axis-ratio, all of which, according to Penfield and Minor, vary with the proportion of hydroxyl in the topaz molecule.

Assuming, with Jannasch[128], that the hydroxyl groups in topaz may be replaced by fluorine, or *vice versa*, regarding the Stadler topaz :



as the mother-substance and replacing the fluorine in the latter by hydroxyl groups, the formulæ of the following theoretically possible topazes are obtained :

$$Si_6Al_{12}O_{24}Fl(OH)_{11},$$
$$Si_6Al_{12}O_{24}Fl_2(OH)_{10},$$
$$Si_6Al_{12}O_{24}Fl_3(OH)_9,$$
$$Si_6Al_{12}O_{24}Fl_4(OH)_8,$$

.
.
.

$$Si_6Al_{12}O_{24}Fl_{12}.$$

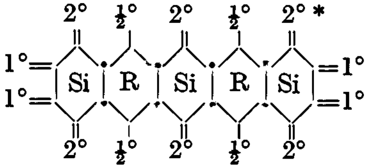
In agreement with this assumption, it has been found by actual analysis that there is a definite maximum proportion of fluorine—no topaz being known which contains a larger percentage than the Städler variety. There also appears to be a minimum, as no topaz is known which contains less than eight atoms of fluorine to six atoms of silica. This interesting result is most easily explained by stating that fluorine atoms which are united to silicon, but not to aluminium (see the structural formula of the Städler topaz), are easily replaced by hydroxyl under natural conditions, or that $\frac{1}{3}$ of the fluorine behaves differently from the remainder.

The probability of the authors' structural formula for topaz is also confirmed by the chemical investigations of Rammelsberg, who observed that on heating topazes to redness, part of the fluorine escapes as silicon fluoride and part as aluminium fluoride.

Further investigations must show that the ratio of the fluorine lost in the form of silicon fluoride to that lost as aluminium fluoride is 1 : 2.

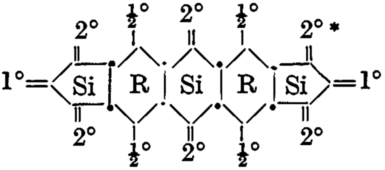
The prognoses of types V and VI are partially confirmed by a re-calculation of the analyses (see *Appendix*) of a number of granites[129] by K. H. Schnerr.

This re-calculation gives the following formulæ :



$18\,RO \cdot 6\,R_2O_3 \cdot 18\,SiO_2$

A.



$16\,RO \cdot 6\,R_2O_3 \cdot 16\,SiO_2$

B.

These agree with the theory that $\frac{1}{3}$ of the aluminium behaves differently from the remainder. The aluminium atoms indicated by dots may be replaced by Fe≡ ; compounds of type A may contain a maximum of 4 Fe_2O_3.

Although Schnerr refers to granites in which the whole of the

* It is convenient to represent the atomic groups

$$\begin{matrix}-OR'' \\ -OR''\end{matrix}\Big\rangle O, \qquad \begin{matrix}-O \\ -O\end{matrix}\Big\rangle R'', \qquad -Or\ (r = \tfrac{1}{2}R'')$$

by 2°, 1° and $\frac{1}{2}$° respectively (see also p. 166)

aluminium has been replaced by iron, experience shows that the atoms indicated by dots are the ones most easily replaceable by iron.

It happens that those aluminium atoms in the granites which are the most easily replaceable by iron are the very ones which, in the epidotes, are incapable of substitution, and a closer study of the structural formulæ of these two groups of substances leads to the conclusion that *the epidotes are acid salts* whilst *the granites are basic ones.* The presence of a base weakens the attraction between the silicon and aluminium ring radicles, and thereby facilitates the substitution of the aluminium by iron at the points indicated.

The consequences of the authors' hypotheses mentioned in this section agree with the experimental results of other investigators.

V

From the hexite-pentite hypothesis it follows that there must be a minimum molecular weight for the aluminosilicates. Thus, the formulæ of the compounds

$$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2,$$
$$Na_2O \cdot Al_2O_3 \cdot 3\,SiO_2,$$

must be at least sextupled, and those of

$$Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2,$$
$$Na_2O \cdot Al_2O_3 \cdot 5\,SiO_2, \text{ and}$$
$$Na_2O \cdot Al_2O_3 \cdot 4\,SiO_2,$$

must be at least tripled, in order that they may be represented in accordance with the new theory. How does this agree with the facts ?

In many cases the theoretically minimum molecular weight may be ascertained from an analysis of the substance or from certain definite considerations. In this connection, one of a series of silicates :

$$(a)\quad 0.5\,Na_2O \cdot 2.5\,CaO \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 20\,H_2O = \mathring{R}_5\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right) \cdot 20\,H_2O$$

examined by Lemberg (see *Appendix,* Table II) is interesting.

By treating the silicate (*a*) with salt solutions, Lemberg obtained the following compounds :

$$\text{I.}\quad 3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot H_2O = \mathring{K}_6\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right) \cdot H_2O,$$

$$\text{II.}\quad 3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 13\,H_2O = \mathring{K}_6\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right) \cdot 13\,H_2O,$$

$$\text{III.}\quad 3\,Na_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 8\,H_2O = \mathring{Na}_6\left(\hat{Al}\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right) \cdot 8\,H_2O,$$

IV. $$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 16\,H_2O = \overset{\circ}{Na}_6\left(\hat{Al}\begin{array}{l}\diagup \hat{Si}\\ -\hat{Si}\\ \diagdown \hat{Si}\end{array}\right) \cdot 16\,H_2O.$$

By treating silicate (a) with alkali he obtained

V. $$(3\,Na_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2 \cdot 7.5\,H_2O)_2 = \left\{\overset{\circ}{Na}_6\left(\hat{Al}\begin{array}{l}\diagup \overline{Si}\\ -\overline{Si}\\ \diagdown \overline{Si}\end{array}\right)\right\}_2 \cdot 15\,H_2O,$$

and from the latter and potassium chloride the substance

VI. $$(3\,K_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2 \cdot 1.5\,H_2O)_2 = \left\{\overset{\circ}{K}_6\left(\hat{Al}\begin{array}{l}\diagup \overline{Si}\\ -\overline{Si}\\ \diagdown \overline{Si}\end{array}\right)\right\}_2 \cdot 3\,H_2O.$$

In the case of the compounds I, II, III, IV, and the silicate (a) from which they are derived, the minimum molecular weight may be found from the analyses; the formation of compound V from silicate (a) and of VI from V are quite inexplicable if a smaller molecular weight than is required by the hexite-pentite theory is assumed for compounds V and VI.

A second instance of interest in this connection is the mode of formation of the potassium salt

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot H_2O = \overset{\circ}{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot H_2O,$$

from the sodium salt

$$Na_2O \cdot Al_2O_3 \cdot 4\,SiO_2 \cdot 2\,H_2O,$$

as observed by Lemberg (see *Appendix*, Table II). This can only be understood if the molecular weight of the original material—the sodium salt—is tripled; the theoretically minimum molecular weight is then indicated.

The number of instances in which the theoretically minimum molecular weight may be ascertained from analysis is somewhat large, as may be seen from the authors' re-calculation of the formulæ of a large number of silicate analyses. From the numerous examples available, the new formulæ of the *mesolites* (see *Appendix*) may be mentioned here.

Formulæ of the Mesolites

(a) $$2\,Na_2O \cdot 4\,CaO \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 15\,H_2O$$
$$= \overset{\circ}{Na}_4\overset{\circ}{Ca}_4(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 15\,H_2O,$$

(b) $$(1.5\,Na_2O \cdot 5.5\,CaO \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 22\,H_2O)_2$$
$$= \{\overset{\circ}{Na}_3\overset{\circ}{Ca}_{5.5}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si})\}_2 \cdot 44\,H_2O,$$

(c) $$(Na_2O \cdot 3.5\,CaO \cdot 6\,Al_2O_3 \cdot 17\,SiO_2 \cdot 15\,H_2O)_2$$
$$= \{\overset{\circ}{Na}_2\overset{\circ}{Ca}_{3.5}(\hat{Si} \cdot \hat{Al} \cdot \overline{Si} \cdot \hat{Al} \cdot \hat{Si})\}_2 \cdot 30\,H_2O,$$

(d) $$(2\,Na_2O \cdot 3.5\,CaO \cdot 6\,Al_2O_3 \cdot 17\,SiO_2 \cdot 15\,H_2O)_2$$
$$= \{\overset{\circ}{Na}_4\overset{\circ}{Ca}_{3.5}(\hat{Si} \cdot \hat{Al} \cdot \overline{Si} \cdot \hat{Al} \cdot \hat{Si})\}_2 \cdot 30\,H_2O,$$

(*e*) $2\,Na_2O \cdot 4\,CaO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 \cdot 12\,H_2O$
$= \mathring{Na}_4\mathring{Ca}_4(\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \bar{Si}) \cdot 12\,H_2O,$

(*f*) $2\,Na_2O \cdot 3\,CaO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 \cdot 15\,H_2O$
$= \mathring{Na}_4\mathring{Ca}_3(\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \bar{Si}) \cdot 15\,H_2O,$

(*g*) $2.5\,Na_2O \cdot 3\,CaO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 \cdot 20\,H_2O$
$= \mathring{Na}_5\mathring{Ca}_3(\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \bar{Si}) \cdot 20\,H_2O,$

(*h*) $1.5\,Na_2O \cdot 3\,CaO \cdot 6\,Al_2O_3 \cdot 15\,SiO_2 \cdot 18\,H_2O$
$= \mathring{Na}_3\mathring{Ca}_3(\bar{Si} \cdot \hat{Al} \cdot \bar{Si} \cdot \hat{Al} \cdot \bar{Si}) \cdot 18\,H_2O,$

(*i*) $2.5\,Na_2O \cdot 3\,CaO \cdot 6\,Al_2O_3 \cdot 15\,SiO_2 \cdot 13\,H_2O$
$= \mathring{Na}_5\mathring{Ca}_3(\bar{Si} \cdot \hat{Al} \cdot \bar{Si} \cdot \hat{Al} \cdot \bar{Si}) \cdot 13\,H_2O.$

In all the above mesolitic silicates, with the exception of (*e*), analysis indicates the theoretically minimum molecular weight, and there is no need to doubt that the real minimum agrees with the theoretical one, as otherwise the genetic relationship which is known to exist between these and other members of this group would be inexplicable.

It is, moreover, particularly interesting to observe that Thugutt[180] has, by an entirely different method, reached conclusions regarding the minimum molecular weight of certain aluminosilicates which agree, almost without exception, with the authors' theory. Thugutt's conclusions are also of special value because they are based on the results of actual experiments. On the basis of his previously mentioned researches, Thugutt suggests the following constitutional formula :

$$2\,K_2Al_2Si_3O_{10} \cdot K_2Al_2O_4 \cdot 12\,SiO_2$$

which is equivalent to:

$$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 = \mathring{K}_6\left(\hat{Al} \begin{matrix} \hat{Si} \\ \hat{Si} \\ \hat{Si} \end{matrix}\right),$$

the following for nepheline hydrate :

$$4\,(2\,Na_2Al_2Si_3O_{10} \cdot Na_2Al_2O_4) \cdot 15\,H_2O$$

corresponding to :

$$12\,Na_2O \cdot 12\,Al_2O_3 \cdot 24\,SiO_2 \cdot 15\,H_2O = \{\mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})\}_2 \cdot 15\,H_2O,$$

and the following for potash mica :

(*a*) $K_4H_6Al_{12}Si_{18}O_{60}$
$$= 3\,K_2O \cdot 3\,H_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 = \mathring{K}_6\mathring{H}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}),$$

(*b*) $K_4H_8Al_{12}Si_{18}O_{60}$
$$= 2\,K_2O \cdot 4\,H_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 = \mathring{K}_4\mathring{H}_8(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}).$$

In some silicates the theoretically minimum molecular weight is double that found by Thugutt. Thus, he attributes to potash nepheline the formula :

$$2\,K_2Al_2Si_3O_{10} \cdot K_2Al_2O_4,$$

which, if doubled, gives :

$$6\,K_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{K}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}).$$

The same is true of Thugutt's constitutional formula for potash mica :

$$H_2K_2Al_4Si_6O_{20} \cdot H_2Al_2O_4,$$

which, if doubled, gives :

$$2\,K_2O \cdot 4\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{K}_4\mathring{H}_8(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}).$$

Equally interesting in this connection are the so-called *sodalites.** According to Lemberg's[131] and Thugutt's[132] researches, these are not atomic, but true molecular compounds. This view is opposed to that of other investigators. It is highly probable, from the results of Lemberg's and Thugutt's experiments, that the sodalites are derivatives of the sodium nepheline hydrates, and that they are so constituted that a portion of their "water of crystallisation" appears to be replaceable by various salts. If this is really the case, on decomposition they must be capable of forming products which are identical with those from sodium nepheline hydrate.

Thugutt's researches have shown that, in reality, one-third of the sodium and one-third of the alumina can be removed from the sodalite in the form of aluminate of potash. Natrolite may be formed by the action of potassium carbonate solution, chloride of sodium (or whatever salt may be added) being set free. Thus, the blue chlorosodalite from the eläolite-syenite from Ditró decomposes in accordance with the equation :

$$3\,Na_2Al_2Si_2O_8 \cdot 2\,NaCl + 2\,K_2CO_3 + 6\,H_2O$$
$$= 2\,Na_2CO_3 + 2\,NaCl + 2\,(K_2Al_2Si_3O_{10} \cdot 3\,H_2O) + Na_2Al_2O_4.$$

(*Cf.* the analogous behaviour of nepheline hydrate, p. 61.) As a result of this reaction, Thugutt considers that the formula of chlorosodalite should be :

$$2\,Na_2Al_2Si_3O_{10} \cdot Na_2Al_2O_4 \cdot 2\,NaCl,$$

but as it is a derivative of sodium nepheline hydrate, whose constitutional formula is

$$8\,Na_2Al_2Si_3O_{10} \cdot 4\,Na_2Al_2O_4 \cdot 15\,H_2O,$$

—this being confirmed by its reaction with potassium carbonate—Thugutt's molecular weight of chlorosodalite should be at least quadrupled ; its constitutional formula then becomes :

$$8\,Na_2Al_2Si_3O_{10} \cdot 4\,Na_2Al_2O_4 \cdot 8\,NaCl.$$

If $4\,Na_2SO_4$ replaces the 8 NaCl, the constitutional formula of the sulphatosodalite or norsean is obtained ; if the 8 NaCl is replaced by $4\,Na_2S_2$ that of ultramarine results, and so on. Thugutt has artificially prepared a large number of analogous substances and has allotted molecular weights to them, as shown in the following Table.

* Another means of representing the constitutional formula of the sodalites atomically is possible and is discussed in connection with the ultramarines (p. 152 *et seq.*).

Thugutt's Sodalite Series[133]

$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ NaCl \cdot 4\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 6\ NaBr$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 6\ NaI \cdot 6\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ NaClO_3 \cdot 2\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2O.\ B_2O_3 \cdot 8\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_2O \cdot I_2O_5.\ 10\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ NaClO_4 \cdot 4\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 4\ Na_2CO_3 \cdot 12\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2CO_3 \cdot 18\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 4\ Na_2SiO_3 \cdot 16\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) .\ 3\ Na_2SiO_3 \cdot 15\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 4\ Na_2SO_4 \cdot 12\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2SO_4 \cdot 12\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2CrO_4 \cdot 15\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2SeO_4 \cdot 12\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2MoO_4 \cdot 21\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot Na_2WO_4 \cdot 13\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_4P_2O_5 \cdot 12\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ NaNO_3 \cdot 6\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2O \cdot P_2O_5 \cdot 18\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 4\ Na_2HPO_4 \cdot 14\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_4P_2O_7 \cdot 14\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2O \cdot As_2O_5 \cdot 14\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2S_2O_3 \cdot 9\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ NaOH \cdot 4\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 6\ NaI \cdot 9\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ HCOONa$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 6\ CH_3 \cdot COONa \cdot 3\ H_2O$,
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2C_2O_4 \cdot 18\ H_2O$.

The minimum molecular weight of any member of this series may be ascertained from an analysis of the substance, as in the two following sodalites :—

$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 3\ Na_2O \cdot B_2O_3 \cdot 8\ H_2O$ and
$12\ Na_2O \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot Na_2WO_4 \cdot 13\ H_2O$.

The hexite-pentite theory formulated by the authors of the present volume gives the same molecular weight. Moreover, if the salt-content (in molecules) of a sodalite is represented by

$$m\Sigma$$

and the water-content (in molecules) by

$$nH,$$

the constitution of these substances may be ascertained from the following formula :—

$$\{\mathring{N}a_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})\}_2 \cdot m\Sigma \cdot nH.$$

For some micas, Thugutt[134] suggests constitutional formulæ with a different molecular weight from that implied by the hexite-pentite theory. Thus, he attributes to two potash micas the formulæ :

$K_9H_3Al_{12}Si_{18}O_{60} \cdot H_6Al_6O_{12} = 4.5\ K_2O \cdot 4.5\ H_2O \cdot 9\ Al_2O_3 \cdot 18\ SiO_2$,
$K_6H_6Al_{12}Si_{18}O_{60} \cdot H_6Al_6O_{12} = 3\ K_2O \cdot 6\ H_2O \cdot 9\ Al_2O_3 \cdot 18\ SiO_2$,

whilst the authors of the hexite-pentite theory prefer:

$$3\,K_2O \cdot 3\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{K}_6\mathring{H}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}), \text{ and}$$
$$2\,K_2O \cdot 4\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{K}_4\mathring{H}_8(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}).$$

This contradiction is more apparent than real, and the fact that $\frac{1}{3}$ of the aluminium in these compounds behaves differently from the remainder is equally well shown in the authors' formulæ. Indeed, there appears to be no important reason why Thugutt should not substitute the formulæ:

$$K_6H_2Al_8Si_{12}O_{40} \cdot H_4Al_4O_8, \text{ and}$$
$$K_4H_4Al_8Si_{12}O_{40} \cdot H_4Al_4O_8,$$

for those he has selected, and so obtain formulæ which give the same molecular weight as those suggested by the authors.

Another apparent contradiction to the authors' theory is the nepheline formula calculated by Thugutt from a series of analyses in Hintze's "Handbuch." In this calculation, notwithstanding that he has represented nepheline hydrate and potash nepheline by formulæ in which the alumina-silica ratio is 1 : 2, and the great probability that in nepheline itself this ratio is also 1 : 2, Thugutt selects the formula:

$$K_2Na_8Al_{10}Si_{11}O_{42} = K_2O \cdot 4\,Na_2O \cdot 5\,Al_2O_3 \cdot 11\,SiO_2;$$

and in accordance with the reaction of this substance with alkaline carbonates he gives

$$8\,Na_2Al_2Si_3O_{10} \cdot 4\,Na_2Al_2O_4 \cdot 3\,K_2Al_2Si_3O_{10}$$

as the constitutional formula.

This formula is quite inexplicable by the hexite-pentite theory.

As a matter of fact, the nepheline analyses by Hintze[185] do not yield a formula in which the alumina-silica ratio is 1 : 2. Several analyses approach very closely to the formula:

$$K_2O \cdot 4\,Na_2O \cdot 5\,Al_2O_3 \cdot 12\,SiO_2 = \mathring{K}_2\mathring{Na}_8(\hat{Si} \cdot \overline{Al} \cdot \overline{Al} \cdot \hat{Si}).$$

Molecular Weights		Calculated Composition	Analyses XXIII	XXV	XXIV
K_2O =	94	5.98%	5.66%	4.76%	5.05%
$4\,Na_2O$ =	248	15.77%	15.71%	15.97%	16.35%
$5\,Al_2O_3$ =	510	32.45%	32.66%	32.06%	33.28%
$12\,SiO_2$ =	720	45.80%	45.23%	45.53%	45.10%
	1572	100.00%			

It is conceivable that the decomposition products of nepheline must be the same as those of nepheline hydrate, as its constitution is analogous, even though it contains a different alumina-silica ratio.

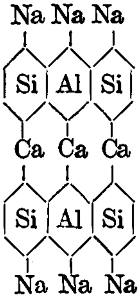
Thus, the consequences of the hexite-pentite theory do not, as regards minimum molecular weight, contradict the facts.

VI

The conclusion has already (see pp. 22 to 26) been reached that, of all the theories devised for showing the constitution of the alumino-silicates, the one which agrees best with the facts is that which assumes that these compounds are complex acids and their corresponding salts.

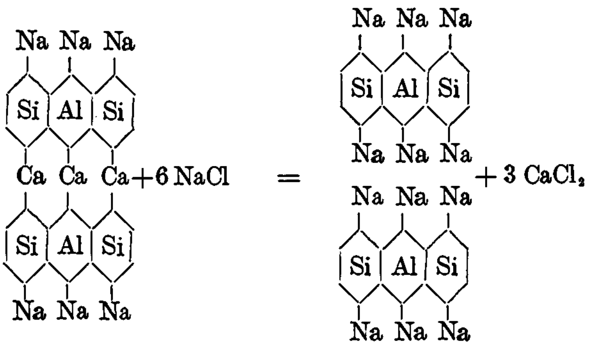
It has also been shown that, by the use of the hexite hypothesis respecting the arrangement of the atoms, most of the objections to the "complex acid theory" disappear. Thugutt's discovery that part of the aluminium behaves differently from the remainder and that of P. Silber that in nepheline $\frac{1}{3}$ of the sodium behaves differently from the other $\frac{2}{3}$ are not only explicable, but are direct consequences of the theory. A complete classification of a large number of alumino-silicates is also rendered possible; the felspars, micas, scapolites, etc. need no longer be regarded as belonging to different groups of minerals, but may be considered all to belong to a single class of compounds. They can only be conceived as salts of a definite series of alumino-silicic acids, and the "mixture theory" may be abandoned.

Only the behaviour of andesite now remains unexplained, and even this will become clear if the following constitutional formula—based on the hexite-pentite theory—is used:



$$3\,Na_2O \cdot 3\,CaO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2.$$

A glance at this structural formula of andesite shows that it will react with NaCl as shown by the following equation:



The complex is decomposed and the re-formation of andesite by means of $CaCl_2$ (double decomposition) is impossible.

The conception of the aluminosilicates as complex acids thus agrees excellently with experimental results.

VII

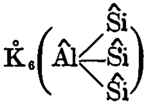
From the structural formulæ already given it follows that two kinds of isomerism[136] * are possible :

1. An isomerism resulting from a different, yet still symmetrical, arrangement of the basal atoms, or " Basis-isomerism," and
2. An isomerism due to the ring radicles, or " Ring-isomerism."

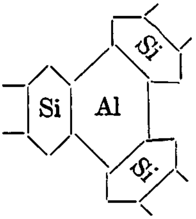
A few examples will make this clearer :

I. Basis isomerism

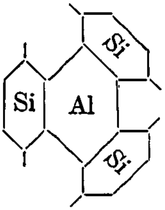
From the compound



two isomers are possible :



I.

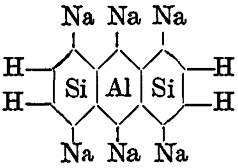


II.

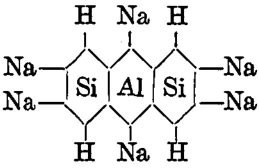
From the compound

$$\mathring{H}_4\mathring{Na}_6(\hat{Si}\cdot\hat{Al}\cdot\hat{Si}),$$

two basis-isomers are also possible :



I.

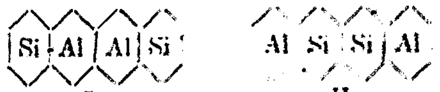


II.

* For Literature with reference to Isomerism in inorganic compounds see No. 136 in Bibliography.

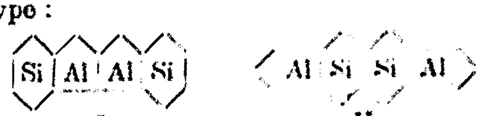
II. Ring isomerism

From compounds with an alumina-silica ratio of 1 : 2, two ring-isomers are possible :

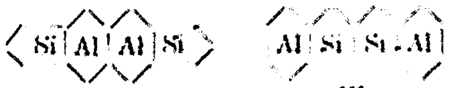


I. II.

From the derivatives of this type, analogous ring-isomers produce a secondary type :

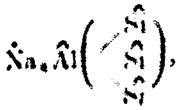


I. II.



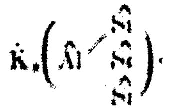
III. IV. etc.

Crystallographic and chemical investigations have already indicated the actual existence of isomeric aluminosilicates. Thus, potash felspar



is already known in two forms, viz. as orthoclase (monoclinic) and microcline (triclinic).

Soda felspar,



is also known to occur in the two forms of sodium orthoclase (monoclinic) and albite (triclinic).

The following results of work by Thugutt confirm the existence of ring-isomers: In the previous Section it was shown that the constitutional formula of the sodalites is based upon

$$\{\dot{Na}_{11}(\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si})\}_2 \cdot m\,\Sigma \cdot n\,H.$$

Hence the existence of a second series of sodalites with the formula

$$\{\dot{Na}_{11}(\hat{Al}\cdot\hat{Si}\cdot\hat{Si}\cdot\hat{Al})\}_2 \cdot m\,\Sigma \cdot n\,H,$$

is theoretically possible. As a matter of fact, Thugutt has discovered two chlorosodalites with a different behaviour towards calcium chloride, although the chemical composition of both is identical.

The artificially prepared hydrogen sodalite behaves towards calcium chloride in a manner quite different from that of the natural sodalites from Arendal, Ditró, Miask, and Turkestan.

The artificial variety, on treatment with calcium chloride solution, yields a calcium chloride-sodalite according to the following equation :

$$3\,(6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 4\,NaCl) + 22\,CaCl_2$$
$$= 3\,(6\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 4\,CaCl_2 + 48\,NaCl.$$

With natural sodalites, on the contrary, the equation is :

$$2\,(6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 4\,NaCl) + 12\,CaCl_2$$
$$= 2\,(6\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2) + 32\,NaCl.$$

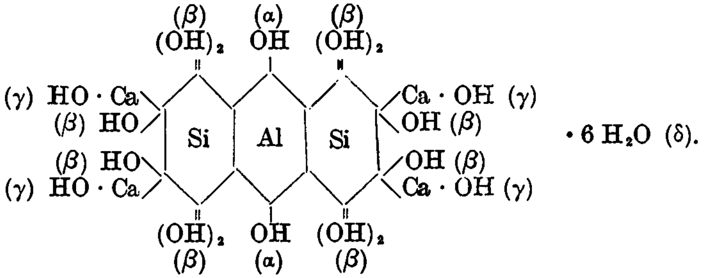
It is, at present, impossible to say which formula belongs to either of the two isomers.

Further researches will show how far these prognoses of the theory are confirmed in this respect by the facts.

VIII

Water may be present either as "water of crystallisation" or "water of constitution," the latter being acid- or base-water. The "acid-water" may be of various kinds : part of the hydroxyl groups may be united to the aluminium hexite or pentite, the remainder to the silicon hexite or pentite.

This may be seen from the following formula, in which the different kinds of water are indicated by α, β, γ, and δ, respectively :



Since Damour first drew attention to the change in the behaviour of the water in hydrous aluminosilicates or zeolites at higher temperatures, this subject has been studied by various investigators (see p. 4, last line) and particularly by Clarke.

Of the zeolites examined by Clarke[138], those relevant to the present purpose are laumontite, thomsonite, hydronephelite, heulandite, epistilbite, stilbite, faujasite, scolecite, foresite, and natrolite.

The Structural Formulæ of the above-mentioned Zeolites, based on their behaviour at high temperatures (after Clarke)

I. Laumonite

$$Al_4(SiO_4)_5 \cdot Si_3O_8 \cdot Ca_2H_8 \cdot 4\,H_2O = 4\,H_2O \cdot 2\,CaO \cdot 2\,Al_2O_3 \cdot 8\,SiO_2 \cdot 4\,H_2O.$$

II. Thomsonite

$$Al_4(SiO_4)_6Ca_3(AlH_2O_2)_2H_4 \cdot 3\,H_2O$$
$$= 4\,H_2O \cdot 3\,CaO \cdot 3\,Al_2O_3 \cdot 6\,SiO_2 \cdot 3\,H_2O.$$

These structural formulæ were suggested by Clarke from a study of the dehydration experiments of Damour, Hersch, and others, which showed that $\frac{4}{7}$ of the water must be regarded as "water of constitution."

III. Hydronephelite

$$Al_3(SiO_4)_3 \cdot Na_2H \cdot 3\,H_2O$$
$$= \tfrac{1}{2}\,(2\,Na_2O \cdot H_2O \cdot 3\,Al_2O_3 \cdot 6\,SiO_2 \cdot 6\,H_2O).$$

IV. Heulandite

$$Al_4(SiO_4)_3(Si_3O_8)_3Ca_2H_8 \cdot 6\,H_2O$$
$$= 4\,H_2O \cdot 2\,CaO \cdot 2\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O.$$

V. Epistilbite

$$Al_4(SiO_4)_3(Si_3O_8)_3Ca_2H_8 \cdot 6\,H_2O$$
$$= 4\,H_2O \cdot 2\,CaO \cdot 2\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O.$$

Epistilbite is stated by Clarke to have the same composition as heulandite, but the water in it appears to be more strongly bound.

VI. Stilbite

Of the same composition as epistilbite and heulandite; behaves like heulandite on fusion, but sometimes forms anorthite.

VII. Faujasite

$$Al_4(SiO_4)_4(Si_3O_8)_2Na_2CaH_8 \cdot 15\,H_2O$$
$$= 4\,H_2O \cdot Na_2O \cdot CaO \cdot 2\,Al_2O_3 \cdot 10\,SiO_2 \cdot 15\,H_2O.$$

VIII. Scolecite

$$Al_4(SiO_4)_6Ca_2H_8 \cdot 2\,H_2O = 4\,H_2O \cdot 2\,CaO \cdot 2\,Al_2O_3 \cdot 6\,SiO_2 \cdot 2\,H_2O.$$

IX. Foresite

$$Al_4(SiO_4)_6CaH_3 \cdot H_2O = 4\,H_2O \cdot CaO \cdot 2\,Al_2O_3 \cdot 6\,SiO_2\,H_2O.$$

X. Natrolite

$$Al_2(SiO_4)_3Na_2H_4 = 2\,H_2O \cdot Na_2O \cdot Al_2O_3 \cdot 3\,SiO_2.$$

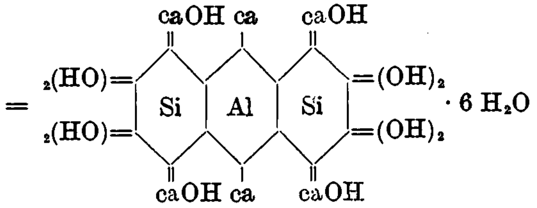
The Structural Formulæ of Laumontite, Thomsonite, etc., according to the Hexite-Pentite Theory

The structural formulæ suggested by Clarke, when rearranged in accordance with the hexite-pentite theory, yield constitutional formulæ in which the results of Clarke's researches may also be seen, as follows:

I. Laumontite

Clarke's formula multiplied by $\frac{3}{2}$ gives:

$$6\,H_2O \cdot 3\,CaO \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \mathring{H}_{12}\mathring{C}a_3(\hat{S}i \cdot \hat{A}l \cdot \hat{S}i) \cdot 6\,H_2O$$

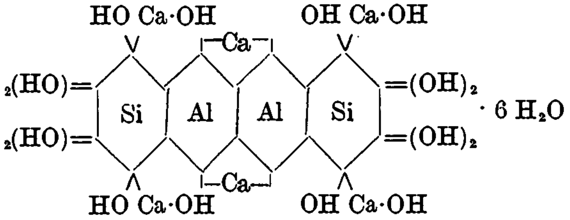


ca = ½ Ca

II. Thomsonite

Clarke's formula multiplied by 2 gives :

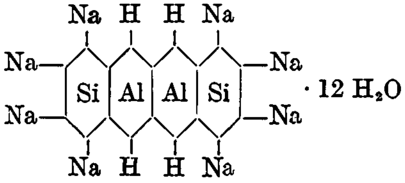
$$8\,H_2O \cdot 6\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O = \mathring{H}_{16}\mathring{C}a_6(\hat{S}i \cdot \hat{A}l \cdot \hat{A}l \cdot \hat{S}i) \cdot 6\,H_2O$$



III. Hydronephelite

Clarke's formula multiplied by 4 gives :

$$4\,Na_2O \cdot 2\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 12\,H_2O = \mathring{H}_4\mathring{N}a_8(\hat{S}i \cdot \hat{A}l \cdot \hat{A}l \cdot \hat{S}i) \cdot 12H_2O$$

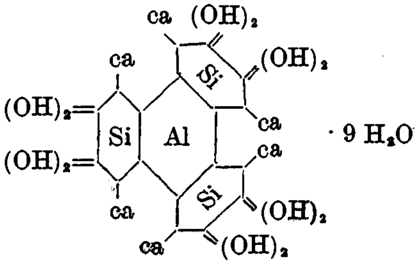


Ring- and Base-isomers of this composition are clearly possible.

IV. Heulandite

Clarke's formula multiplied by ¾ gives :

$$6\,H_2O \cdot 3\,CaO \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot 9\,H_2O = \mathring{H}_{12}\mathring{C}a_3\left(\hat{A}l \begin{smallmatrix}\hat{S}i \\ \hat{S}i \\ \hat{S}i\end{smallmatrix}\right) \cdot 9\,H_2O$$

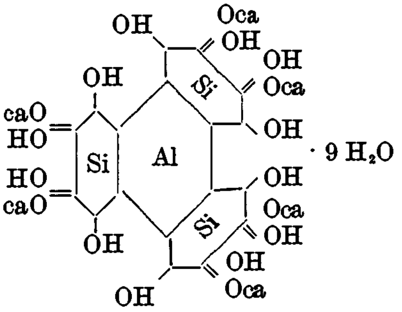


ca = ½ Ca

V. Epistilbite

Epistilbite, according to Clarke, has the same composition as heulandite, but the water is more strongly bound.

Possibly epistilbite has the following structural formula :



ca = ½ Ca

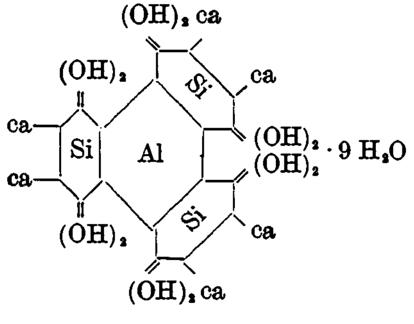
as in this the water would be bound more strongly than in heulandite.

VI. Stilbite

Clarke's formula multiplied by $\frac{3}{2}$ may be expressed thus :

$$6\ H_2O \cdot 3\ CaO \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 9\ H_2O = \mathring{H}_{12}\mathring{C}a_3\left(\hat{A}l\begin{matrix}\hat{S}i\\ \hat{S}i\\ \hat{S}i\end{matrix}\right) \cdot 9\ H_2O.$$

Stilbite is either analogous to heulandite or epistilbite or it is an isomeric product of heulandite with the following formula :



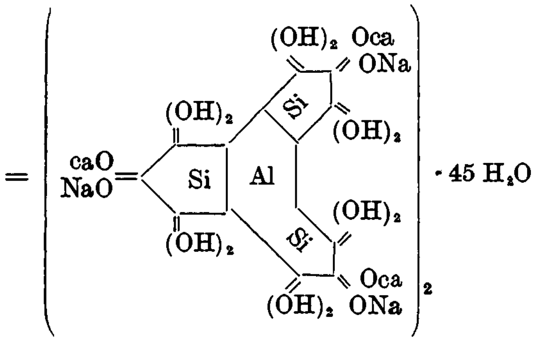
ca = ½ Ca

VII. Faujasite

Clarke's formula multiplied first by $\frac{3}{2}$ and then by 2 gives :

$$(6\ H_2O \cdot 1.5\ CaO \cdot 1.5\ Na_2O \cdot 3\ Al_2O_3 \cdot 15\ SiO_2 \cdot 22.5\ H_2O)_2$$

$$= \left\{\mathring{H}_{12}\mathring{N}a_3\mathring{C}a_{1\cdot 5}\left(\hat{A}l\begin{matrix}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{matrix}\right)\right\}_2 \cdot 45\ H_2O$$

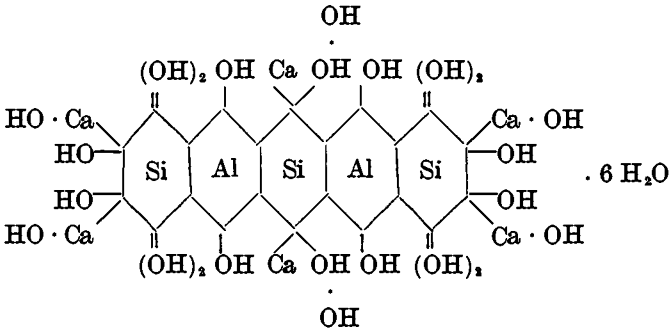


ca = $\frac{1}{2}$ Ca

VIII. Scolecite

Clarke's formula multiplied by 3 gives :

$$12\,H_2O \cdot 6\,CaO \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 6\,H_2O$$
$$= \mathring{H}_{24}\mathring{C}a_6(\hat{S}i \cdot \hat{A}l \cdot \hat{S}i \cdot \hat{A}l \cdot \hat{S}i) \cdot 6\,H_2O$$

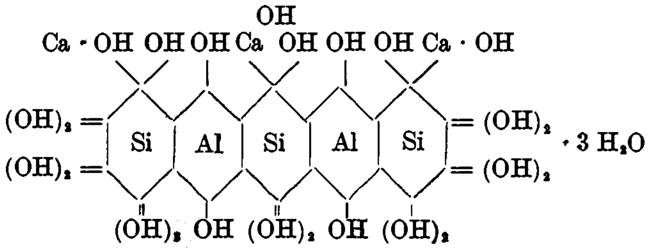


Scolecite is of special interest, inasmuch as it must contain all the four different kinds of theoretically possible water.

IX. Foresite

If Clarke's formula is tripled it gives :

$$12\,H_2O \cdot 3\,CaO \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 3\,H_2O$$
$$= \mathring{H}_{24}\mathring{C}a_3(\hat{S}i \cdot \hat{A}l \cdot \hat{S}i \cdot \hat{A}l \cdot \hat{S}i) \cdot 3\,H_2O$$



Foresite contains all the four kinds of water theoretically possible.

X. Natrolite

Clarke's formula, if multiplied by 6, leads to one which is impossible according to the hexite-pentite theory, as compounds with an alumina-silica ratio of 1 : 3 cannot have more than 12 R_2O. This does not necessarily prove an objection to the theory, as Clarke, in publishing his formula for natrolite, definitely pointed out that the character of the water in this compound is doubtful.

Further investigations will show that this compound only contains 6 molecules of "water of constitution."

The Hexite-Pentite Theory and other Zeolites

Part of the prognosis of the theory put forward by the authors of this volume is completely confirmed by the facts ; it will, therefore, be of special interest to enquire whether other investigations of zeolites—such as fractional determination of water—will lead to the same conclusions as to the existence of water in four different forms of combination in such compounds as scolecite, foresite, etc.

A number of investigators, following the researches of Friedel, E. Mallard and E. Rinne[733], have concluded that the zeolites form a remarkable class of substances which differ from the hydrates. The work of A. Damours, who showed that water can be partially absorbed by dehydrated zeolites re-combined, supports this conclusion. There is a general impression that the loss of water from zeolites does not follow the laws of Dalton and Proust, though this view is in direct contradiction to the experiments of Clarke. This view has been specially supported by J. M. van Bemmelen[717], E. Doelter[733], F. Rinne[718], and Sommerfeldt[719], but A. Johnson[720] adopts the contrary view and maintains that the evolution of water is not, in principle, different from that of normal hydrates.

J. M. van Bemmelen regarded the combination of water in zeolites as similar to that in silica jellies. Doelter regards it as "adsorbed." E. Rinne has found, in the case of heulandite and desmine, that definite changes in the water-content are accompanied by equally definite changes in the optical character of these substances. According to him, in heulandite and desmine an equilibrium is formed at all temperatures and the loss of water is dependent on external circumstances such as atmospheric pressure and temperature.

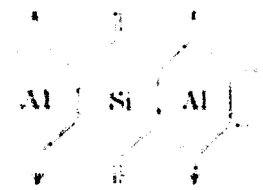
The belief that loss of water by zeolites does not follow stoichiometrical laws is, without doubt, based on an error. Clarke, for instance, has conclusively shown that, in the case of heulandite, the loss of water is quite in accordance with these laws and that in the case of desmine the same regularity is highly probable. The apparent irregularities are due to the use of too small molecular weights for these

compounds, whereby the regularity of the loss may be overlooked. That this is the case with heulandite has already been shown. That it applies equally to desmine is not difficult to prove, as follows:

Desmine has the general formula

$$CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 5\,H_2O.$$

According to the H.P. theory, part of the water shown is "water of constitution" and the remainder is "water of crystallisation" (p. 65), the structural formula being:



$$5\,H_2O \cdot 6\,CaO \cdot 6\,Al_2O_3 \cdot 6\,SiO_2 \cdot 4\,(6\,H_2O).$$

It is clear that a whole series of water-separation phases may occur, such as:

1. Conversion of two hexites into pentites.
2. Conversion of the remaining hexite into pentite.
3. Separation of four pentites.
4. Separation of four hydroxyl groups.

There are at least ten phases of water-separation which lead to forms differing from each other in crystallographic and optical characters. In short, the researches of Rinne, rightly considered, really agree with the consequences of the H.P. theory.

The compounds

A. $(CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 5\,H_2O)_4$
B. $(CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4\,H_2O)_4$
C. $(CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 3\,H_2O)_4$
D. $(CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 2\,H_2O)_4$
E. $(CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O)_4$
F. $(CaO \cdot Al_2O_3 \cdot SiO_2)_4$

are distinguished by their different optical and crystallographic properties, the compounds A, B, and C being monoclinic, D appears to be rhombic, E still more clearly rhombic, and F (which has no water of constitution) is amorphous.

Sommerfeldt considers that the zeolites, unlike the hydrates, lose water continuously, and regards them as solid solutions. He has applied the law of Ch. Henry and the second law of thermodynamics to zeolites by integration, and the substitution of logarithms for natural numbers in the formula:

$$\text{(1)} \qquad U = \frac{-RT^2\, d\left(\ln \frac{c'}{c}\right)}{dT}$$

in which the concentration of the water in the solid and vaporous form is represented by c' and c. He devised a second formula in which at least two temperatures are known and are proportionate to the maximal tensions of the water vapour and that of the water occluded in unit volume of the substance, namely $c_2' : c_2$. The heat of combination may, in this way, be calculated.

From the formula thus obtained

$$(2) \qquad U = +\ 4{\cdot}584 \log.\left(\frac{c'_1}{c_1}\,\frac{c_2}{c'_2}\right)\frac{T_1\ T_2}{T_2 - T_1} \text{ Calories,}$$

it is possible to ascertain whether the usual laws of thermodynamics are applicable to zeolites. If, for instance, the vapour tension of the occluded water c' and the heat of combination U in the formula (2) are sufficient, the zeolites may be regarded as solid solutions. E. Sommerfeldt has determined calorimetrically the evolution of heat, U, following the absorption of water by analcime, and obtained, as the result of three tests, the values 1520, 1710, and 1635 Cals. for the heat of combination of 1 molecule of water, i.e. an average of 1622 Cals. From the percentage of water by weight which a sample of analcime lost on being heated from 20° to T° C., whereby it is in equilibrium with the water vapour, the maximum temperature of which can be ascertained from G. Friedel's researches, the heat of combination U may be found to be approximately 8530 Cals. This disagreement shows that the formula (2) cannot be applied to zeolites. Hence, according to E. Sommerfeldt, zeolites cannot be solid solutions; he regards them as adsorption products.

This conclusion of Sommerfeldt's is only partially correct, as the disagreement of the value found with that calculated merely shows that the zeolites are not solid solutions. It does *not* show that the water is adsorbed, i.e. combined in non-stoichiometric proportions. Indeed, the authors of the present volume have previously shown that the available experimental material only indicates that the zeolites do not differ essentially from other hydrates.

The objection may be raised that the chief characteristic of zeolites—their ability to re-combine with water of crystallisation, as shown by Damour, whereby they are distinguished from other compounds containing water of crystallisation—is inexplicable in terms of the H.P. theory. This anomaly is, however, merely superficial. The power of combining with water has been exhaustively shown, elsewhere, to be due to:

1. The number of hydroxyl groups belonging to the water of crystallisation, and
2. The nature of the base in compounds (salts).

The more hydroxyl groups a compound contains, the closer is its relationship to ring-water. In saline compounds the combining power of the ring-water is also dependent on the nature of the base. Some complex acids have a close relationship to ring-water and therefore

crystallise with a relatively large number of water-rings. The sodium salts of these acids contain less water of crystallisation, the potassium salts still less; hence the water of crystallisation in the sodium compounds is more strongly combined than in the analogous potassium salts. It is, in fact, probable that the calcium group (O.Ca.OH) near the OH groups in zeolites causes the water-rings which have been separated to re-combine. This property of re-combination—so characteristic of zeolites—cannot properly be made a reason for separating these compounds from others containing water of crystallisation, and forming a separate class of compounds of a so-called "zeolitic character."

IX

The hexite-pentite theory proposed by the authors enables prognoses of the chemical composition of the aluminosilicates to be made. Two kinds of prognoses must be clearly distinguished:

1. Those founded on the proportion of base in the compound (Base-prognoses) and
2. Those involving the presence of ring radicles (Ring-prognoses).

1. Base-prognoses

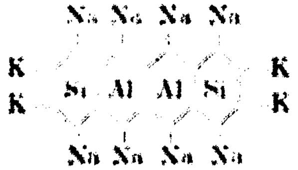
From a study of formulæ of the type

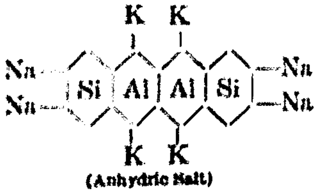
$$Si \cdot \dot{Al} \cdot \dot{Al} \cdot Si = 6\,Al_2O_3 \cdot 12\,SiO_2,$$

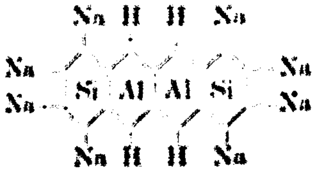
it is possible to predict that

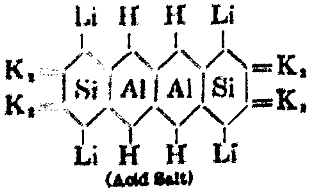
1. Compounds having such a formula can at most contain $10\,R_2O$, and that
2. From formulæ of this type the composition of an enormous variety of salts can be predicted, including normal, acid, basic or mixed salts, some already known and others the existence of which has yet to be proved. By replacing the hydroxyl groups by halogens a further series of compounds is theoretically possible.

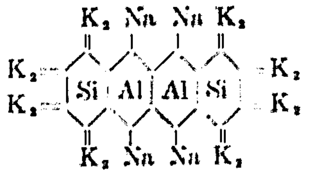
Thus, the existence of the following compounds of this type is readily conceivable; the same is true of other formulæ:

1. 
(Normal Salt)

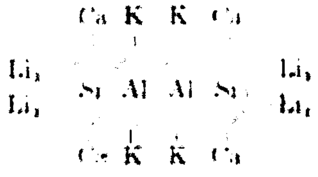
2. 
(Anhydric Salt)

3. 
(Acid Salt)

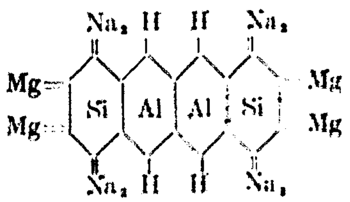
4. 
(Acid Salt)

5. 

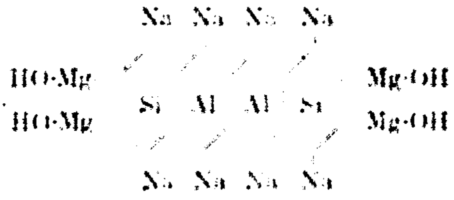
(Normal Salt)

6. 

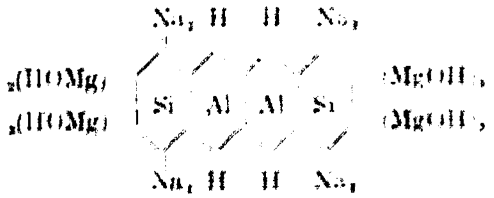
(Normal Salt)

7. 

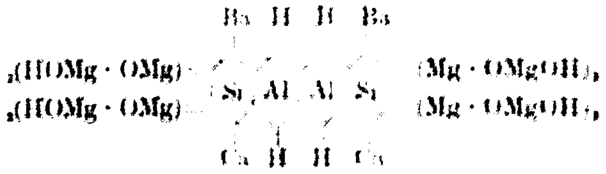
(Acid Salt)

8. 

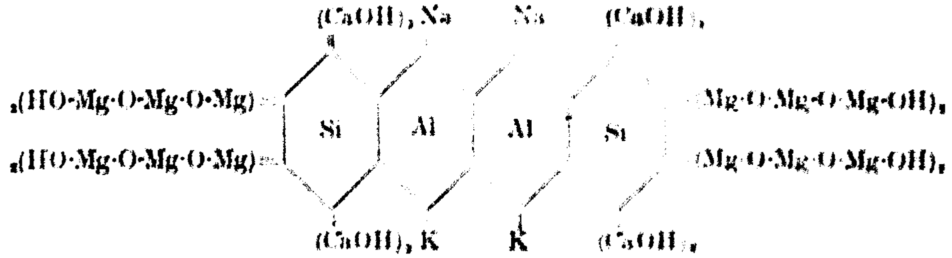
(Basic Salt)

9. 

(Acid and Basic Salt)

10. 

(Acid and Basic Salt)

11. 

2. Ring-prognoses

From each primary type of formula, a series of secondary compounds may be devised. Thus, from the primary type :

$$\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si}$$

the secondary (a) $\bar{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \bar{Si}$, and
(b) $\hat{Si} \cdot \bar{Al} \cdot \bar{Al} \cdot \hat{Si}$, may be produced;

from the primary: $\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}$

the secondary: (a) $\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \bar{Si}$,
(b) $\bar{Si} \cdot \hat{Al} \cdot \bar{Si} \cdot \hat{Al} \cdot \bar{Si}$,
(c) $\hat{Si} \cdot \bar{Al} \cdot \hat{Si} \cdot \bar{Al} \cdot \hat{Si}$,.
(d) $\bar{Si} \cdot \bar{Al} \cdot \hat{Si} \cdot \bar{Al} \cdot \bar{Si}$,
etc.

It has already been shown that a portion of the aluminium in epidote is replaceable by $Fe\equiv$. From the formula for tourmaline (see *Appendix*) it may be concluded that part of the aluminium in aluminosilicates is replaceable by boron. If it be admitted that the aluminium in hexites and pentites may be replaced, in whole or in part, by elements capable of forming sesquioxides—and this view is highly probable and is supported by many analyses—the constitution of a large number of compounds may be represented.

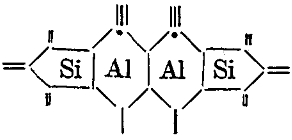
An interesting series of prognoses may be based on the properties of the mineral "ardennite,"[151] in which part of the aluminium is replaced by vanadium. The composition of this mineral is shown by the formula:

$$10\,MnO \cdot V_2O_5 \cdot 5\,Al_2O_3 \cdot 10\,SiO_2 \cdot 5\,H_2O,$$

which may be derived from:

$$\bar{Si} \cdot \hat{R} \cdot \hat{R} \cdot \bar{Si}$$

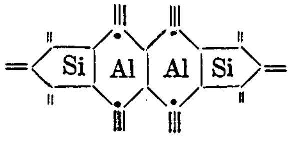
the structural formula being



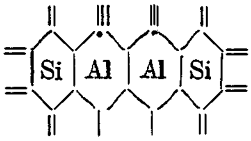
$\cdot\, 5\,H_2O = 10\,RO \cdot V_2O_5 \cdot 5\,Al_2O_3 \cdot 10\,SiO_2 \cdot 5\,H_2O.$

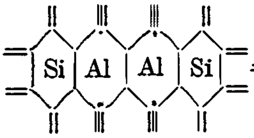
The positions indicated by dots show the vanadium atoms in the aluminium hexite. Vanadium hydrate is $Vd \equiv (OH)_5$, hence the trivalency of the dotted positions.

It is highly probable that other "ardennites" will be found, including the following:

1. 

$\cdot\, aq. = 12\,R_2O \cdot 2\,V_2O_5 \cdot 4\,Al_2O_3 \cdot 10\,SiO_2 \cdot aq.$

2.  $\cdot aq. = 12\,R_2O \cdot V_2O_5 \cdot 5\,Al_2O_3 \cdot 12\,SiO_2 \cdot aq.$

3.  $= \cdot aq. = 14\,R_2O \cdot 2\,V_2O_5 \cdot 4\,Al_2O_3 \cdot 12\,SiO_2 \cdot aq.$

etc.

The replacement of the silicon by allied elements, such as titanium, zirconium, tin, etc., is also possible, and a further large variety of compounds becomes conceivable. For instance, in the formula

$$(a)\quad \hat{Al} \cdot \hat{Si} \cdot \hat{Al},$$

the aluminium atoms may be replaced by those of boron to produce

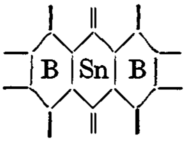
$$(b)\quad \hat{B} \cdot \hat{Si} \cdot \hat{B}.$$

If the silicon in (*b*) is replaced by $\hat{Sn}$

$$\hat{B} \cdot \hat{Sn} \cdot \hat{B},$$

may be produced. In a similar manner, by replacing aluminium and silicon in substances of other types, a large number of borosilicates, aluminostannates and borostannates become theoretically possible.

Few such compounds are known actually to exist ; among others is nordenskiöldite[152]

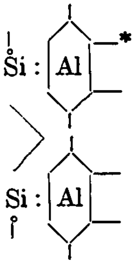


$$6\,CaO \cdot 6\,B_2O_3 \cdot 6\,SnO_2 = \mathring{Ca}_6(\hat{B} \cdot \hat{Sn} \cdot \hat{B}).$$

Apart from those aluminosilicates whose constitution has already been described under the term "α-complexes," there is a smaller series—the "β-complexes"—which must be represented somewhat differently, though they are quite analogous to those previously mentioned. These include sapphirin[153]

$$5\,MgO \cdot 2\,SiO_2 \cdot 6\,Al_2O_3.$$

The constitution of this compound needs some explanation, as it has already (p. 35) been suggested that a silicon hexite can, at most, unite with three $\hat{Al}$. Hence the formula :



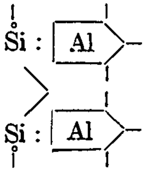
$\overset{\circ}{R}_{10}(\hat{Al} \cdot \overset{\circ}{Si}_2 \cdot \hat{Al})$; $R_2 = Mg$.

Sapphirin must, in fact, be regarded as a salt of an acid derived from the hydrate :

$$\begin{array}{l} Si \equiv (OH)_3, \\ > O \\ Si \equiv (OH)_3 \end{array}$$

and from two hydro-aluminium-hexites by the removal of the elements of water.

Theoretically, a sapphirin corresponding to



$\overset{\circ}{R}_8(\overline{Al} \cdot \overset{\circ}{Si}_2 \cdot \overline{Al})$; $R_2 = Mg$,

is possible, and, as a matter of fact, an analysis by Damour[154] and another by W. Schluttig[155] suggest a sapphirin corresponding to

$$4\,MgO \cdot 2\,SiO_2 \cdot 5\,Al_2O_3.$$

If the aluminium in sapphirin is replaced by

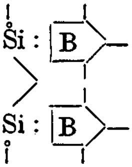
$$Fe \equiv,\ Cr \equiv,\ Mn \equiv,\ B \equiv,\ \text{etc},$$

and the silicon by

$$Ti,\ Zr,\ Sn,\ \text{etc.},$$

a large number of new substances will be formed.

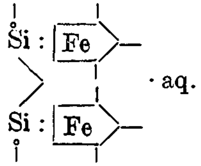
Howlite[156] :



$\overset{\circ}{R}_8(\overline{B} \cdot \overset{\circ}{Si}_2 \cdot \overline{B}) \cdot aq. = 4\,CaO \cdot 2\,SiO_2 \cdot 5\,B_2O_3 \cdot aq.$,

* In this structural formula, the oxygen atoms are omitted for the sake of greater clearness.

and Avasite[157]:



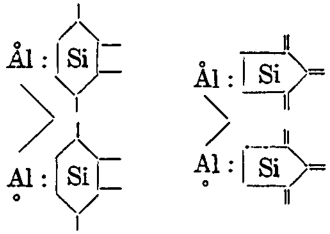
$$\overset{\circ}{H}_8(\overline{Fe}\cdot\overset{\circ}{Si}_2\cdot\overline{Fe})\cdot 5\,H_2O = 4\,H_2O\cdot 2\,SiO_2\cdot 5\,Fe_2O_3\cdot 5\,H_2O,$$

are of this nature.

Theoretically, another class of β-complexes is also possible, viz. those producible from the hydrate

$$\begin{array}{l} Al = (OH)_2 \\ >O \\ Al = (OH)_2 \end{array}$$

and forming silicon hydrohexites and hydropentites in the manner previously described. Compounds of the following types may thus be obtained :



The constitution of the silicates

$2\,CaO\cdot KOH\cdot Al_2O_3\cdot 12\,SiO_2$ (milarite)[158],
$RO\cdot Al_2O_3\cdot 10\,SiO_2\cdot 5\,H_2O$ (ptiolite)[159],
$RO\cdot Al_2O_3\cdot 10\,SiO_2\cdot 7\,H_2O$ (mordennite)[160], etc.,

thus becomes clearer.

X

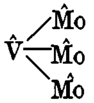
If the molybdenum and tungsten complexes are truly analogous to the aluminosilicates, they must be constituted in an analogous manner. Assuming that, on the one hand, molybdic and tungstic acids and, on the other hand, vanadic, phosphoric, arsenic, and antimonic acids form hexa- and penta-radicles (hexites, pentites, hydrohexites and hydropentites) analogous to the acids of silicon and aluminium, complexes of molybdenum and tungsten together with their compounds must exist or be capable of production, which may be termed α- and

β-complexes ; in other words it must be possible to conceive a large number of molybdic and tungstic complexes whose constitution may be ascertained from the hypothesis just mentioned. It is clear that the chemical properties of the compounds should agree with the structural formulæ assigned to them. That they do so is shown below.

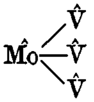
It is now necessary to consider what vanadium molybdates are theoretically possible.

α-Vanadomolybdic anhydrides

$$\hat{Mo} \cdot \hat{V} \cdot \hat{Mo} = 3\,V_2O_5 \cdot 12\,MoO_3,$$
$$\overline{Mo} \cdot \hat{V} \cdot \overline{Mo} = 3\,V_2O_5 \cdot 10\,MoO_3,$$
$$\hat{V} \cdot \hat{Mo} \cdot \hat{V} = 6\,V_2O_5 \cdot 6\,MoO_3,$$
$$\bar{V} \cdot \hat{Mo} \cdot \bar{V} = 5\,V_2O_3 \cdot 6\,MoO_3,$$
$$\hat{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \hat{Mo} = 6\,V_2O_5 \cdot 12\,MoO_3,$$
$$\overline{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \overline{Mo} = 6\,V_2O_5 \cdot 10\,MoO_3,$$
$$\hat{Mo} \cdot \bar{V} \cdot \bar{V} \cdot \hat{Mo} = 5\,V_2O_5 \cdot 12\,MoO_3,$$
$$\hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo} = 6\,V_2O_5 \cdot 18\,MoO_3,$$
$$\overline{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \overline{Mo} = 6\,V_2O_5 \cdot 16\,MoO_3,$$
$$\overline{Mo} \cdot \hat{V} \cdot \overline{Mo} \cdot \hat{V} \cdot \overline{Mo} = 6\,V_2O_5 \cdot 15\,MoO_3,$$
$$\hat{Mo} \cdot \bar{V} \cdot \hat{Mo} \cdot \bar{V} \cdot \hat{M} = 5\,V_2O_5 \cdot 18\,MoO_3,$$
$$\hat{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \hat{V} = 9\,V_2O_5 \cdot 12\,MoO_3,$$
$$\bar{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \bar{V} = 8\,V_2O_5 \cdot 12\,MoO_3,$$
$$\bar{V} \cdot \overline{Mo} \cdot \hat{V} \cdot \overline{Mo} \cdot \bar{V} = 8\,V_2O_5 \cdot 10\,MoO_3,$$



$$= 3\,V_2O_5 \cdot 18\,MoO_3,$$



$$= 9\,V_2O_5 \cdot 6\,MoO_3, \text{ etc. etc.}$$

From the existence of β-aluminosilicates it may be concluded that the existence of analogous β-vanadomolybdates is also theoretically possible. These are formed (1) from the hydrate :

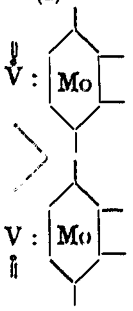
$$V \equiv (OH)_4$$
$$>O$$
$$V \equiv (OH)_4$$

and molybdenum hydrohexites or hydropentites, and (2) from

$$Mo \equiv (OH)_5$$
$$>O$$
$$Mo \equiv (OH)_5,$$

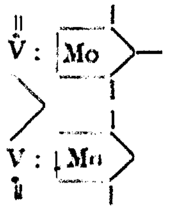
and the corresponding ring-radicles of vanadic acid. In the first case the following hydrates are produced :

(a)



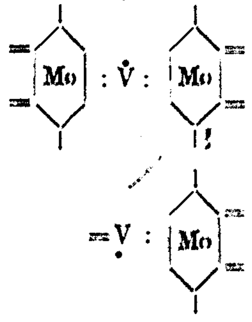
$\dot{H}_{12}(\dot{Mo} \cdot V_2 \cdot Mo)$

(b)



$\dot{H}_{10}(Mo \cdot \dot{V}_2 \cdot Mo)$

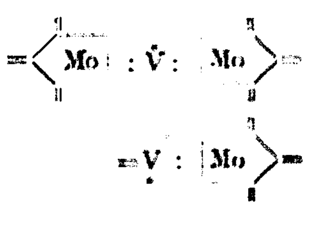
(c)



$\dot{H}_{20}(\dot{V}_2 \langle \dot{Mo}_3)$

$10\ H_2O \cdot V_2O_5 \cdot 18\ MoO_3$

(d)



$\dot{H}_{20}(\dot{V}_2 \langle Mo_3)$

$10\ H_2O \cdot V_2O_5 \cdot 15\ MoO_3$

When the hydrate $OV_2(OH)_8$, like the hydrohexites and hydropentites, forms condensation products, acids of the following anhydrides:

$$6\,V_2O_5 \cdot 16\,MoO_3,$$
$$9\,V_2O_5 \cdot 22\,MoO_3,$$

are formed.

Similarly, a series of β-vanadomolybdates may be formed from $OMo_2(OH)_{10}$ and vanadium hydrohexites or hydropentites.

If, in the α- and β-vanadomolybdates mentioned, the vanadic acids are represented by phosphoric, arsenious, arsenic, antimonious, antimonic, and other acids, and the molybdic acids by tungstic acid, the existence of vanado-, phospho-, arseno-, and other tungstates and of phospho-, arseno-, and other molybdates becomes theoretically possible.

Proofs of the Correctness of the above Formulæ for the Representation of the Chemical Structure of Molybdic and Tungstic Complexes

It has been repeatedly stated in the foregoing pages that the changes which have been observed to occur in Nature in aluminosilicates make it highly probable that under suitable conditions they may be converted into one another. This fact not only agrees with the authors' hexite-pentite theory, but is a natural deduction from the latter. In the case of the various molybdic and tungstic complexes, also, there is the possibility that, with the same component acids, they will be mutually convertible in the widest proportions, if their constitution is analogous to that of the aluminosilicates. For instance, the various vanadomolybdates are, without exception, converted into each other under certain conditions: the vanadotungstates, arsenomolybdates and arsenotungstates are distinguished by this characteristic property.

The best experimental confirmation of the authors' views may be found in the researches of Friedhein and his pupils, whose work is characterised by the great exactitude and care with which it has been carried out.

The above-mentioned property—convertibility—is shown in the Tables on the following pages, in which a number of the results obtained by Friedheim and his pupils have been summarised:

Table A.—Action of a small quantity of MoO_3 on normal vanadates.
Table B.—Action of MoO_3 on normal vanadates.
Table C.—Action of chlorides on $NH_4\,VO_3+MoO_3$.
Table D.—Action of normal vanadates on paramolybdates.
Table E.—Action of MoO_3 on normal vanadates.
Table F.—Action of MoO_3 on phosphates.
Table G.—Action of MoO_3 on arsenates.

Table A. Action of less than 1 mol. MoO_3 on 1 mol. normal Vanadate[161].

Reacting substances	Reaction products: Vanadates	Reaction products: $R_2O \cdot V_2O_5 \cdot MoO_3$	Reaction products: $4\,R_2O \cdot 3\,V_2O_5 \cdot 5\,MoO_3$	Reaction products: $3\,R_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$	Reaction products: $5\,R_2O \cdot 4\,V_2O_5 \cdot 6\,MoO_3$	Relation of the Reaction products, there is formed on decomposition by KCl: $3\,R_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$	Relation of the Reaction products, there is formed on crystallisation: $3\,R_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$
1 Mol. $NH_4VO_3 + \frac{1}{4}$ Mol. MoO_3	—	—	—	—	$5\,(NH_4)_2O \cdot 4\,V_2O_5 \cdot 6\,MoO_3 \cdot 14$ aq.	$3\,K_2O \cdot 2\,V_2O_5\ 4\,MoO_3 \cdot 7$ aq. (for both rows)	$3\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 7$ aq. (for both rows)
1 Mol. $NH_4VO_3 + \frac{1}{2}$ Mol. MoO_3	$(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4$ aq.	—	—	—	$5\,(NH_4)_2O \cdot 4\,V_2O_5 \cdot 6\,MoO_3 \cdot 12$ aq. or 14 aq.		
change of the solution formed from $(NH_4)VO_3 + \frac{3}{4}$ Mol. MoO_3 with Barium chloride in excess	$3\,BaO \cdot 5\,V_2O_5 \cdot 19$ aq.	$BaO \cdot V_2O_5 \cdot MoO_3 \cdot 7$ aq.	—	—	$5\,BaO \cdot 4\,V_2O_5 \cdot 6\,MoO_3 \cdot 28$ aq.	—	—
change of the solution formed from $(NH_4)VO_3 + \frac{3}{4}$ Mol. MoO_3 with Barium chloride not in excess	$(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4$ aq.	—	$3\,(NH_4)_2O \cdot BaO \cdot 3\,V_2O_5 \cdot 5\,MoO_3 \cdot 9$ aq.	—	—	—	—
change of the solution formed from $(NH_4)VO_3 + \frac{3}{4}$ Mol. MoO_3 with KCl in excess	$K_2O \cdot (NH_4)_2O \cdot 4\,V_2O_5 \cdot 8$ aq.	—	$3\,K_2O \cdot (NH_4)_2O \cdot 3\,V_2O_5 \cdot 5\,MoO_3 \cdot 9$ aq.	$2\,K_2O \cdot (NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 5$ aq.	—	—	—
			both substances yield . .		. . . . .	$3\,K_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 7$ aq.	
1 Mol. $(NH_4)VO_3 + \frac{3}{4}$ Mol. MoO_3	$(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4$ aq.	—	—	$3\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot$ aq.	—	$3\,K_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 7$ aq.	$3\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 7$ aq.

Table B.

Action of 1 or more mol. MoO_3 on normal Vanadates[162].

Reacting substances	Reaction products		
$K_2O \cdot V_2O_5 + 3\,MoO_3$	$5\,K_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3$	$2\,K_2O \cdot 2\,V_2O_5 \cdot 5\,MoO_3$	—
$(NH_4)_2O \cdot V_2O_5 + 3\,MoO_3$	—	$2\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 5\,MoO_3$	—
$(NH_4)_2O \cdot V_2O_5 + 2\,MoO_3$	$(NH_4)_2O \cdot V_2O_5 \cdot 3\,MoO_3$	$3\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$	$(NH_4)_2O \cdot 2\,V_2O_5$
$K_2O \cdot V_2O_5 + 2\,MoO_3$	$K_2O \cdot V_2O_5 \cdot 3\,MoO_3$	$5\,K_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3$	—
$Na_2O \cdot V_2O_5 + 2\,MoO_3$	$2\,Na_2O \cdot 3\,V_2O_5$	$2\,Na_2O \cdot V_2O_5 \cdot 6\,MoO_3$	—

Table C.

Conversion of a solution of $NH_4 \cdot VO_3 + MoO_3$ and KCl, NaCl, $BaCl_2$[163].

The Solution of $(NH_4)VO_3$ $+ MoO_3$ gives	Reaction products					
by simple evaporation	$(NH_4)_2O \cdot V_2O_5 \cdot 3\,MoO_3$	—	—	$3\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$	—	acid vanadate
Product with KCl	—	—	$2\,K_2O \cdot V_2O_5 \cdot 6\,MoO_3$	—	—	do.
Product with NaCl	$\left.\begin{matrix}\frac{1}{2}Na_2O\\ \frac{1}{2}(NH_4)_2O\end{matrix}\right\} V_2O_5 \cdot 3\,MoO_3$	—	—	—	—	do.
Product with $BaCl_2$	—	$2\,BaO \cdot V_2O_5 \cdot 3\,MoO_3$*	—	—	$7BaO \cdot 3V_2O_5 \cdot 18MoO_3$	do.

* On crystallisation yields $3\,BaO \cdot 2\,V_2O_5 \cdot 6\,MoO_3$

Table D.

By the action of normal Vanadates on Paramolybdates, the following substances are produced[164]:

Reacting substances	Resulting products			
$2\,KVO_3 + 3\,K_2O \cdot 7\,MoO_3$	$3\,K_2O \cdot V_2O_5 \cdot 6\,MoO_3 \cdot 5\,H_2O$	—	—	—
$2\,NH_4VO_3$ $+ 3\,(NH_4)_2O \cdot 7\,MoO_3$	—	$2\,(NH_4)_2O \cdot V_2O_5$ $\cdot 4\,MoO_3 \cdot 8$ aq.	$2\,(NH_4)_2O \cdot V_2O_5$ $\cdot 3\,MoO_3 \cdot 6$ aq.	—
$4\,NH_4VO_3$ $+ 3\,(NH_4)_2O \cdot 7\,MoO_3$	—	—	$2\,(NH_4)_2O \cdot V_2O_5$ $\cdot 3\,Mo_3O \cdot 6$ aq.	—
Solution of $2\,NaNO_3$ $+ 3\,Na_2O \cdot 7\,MoO_3$ $+ NH_4Cl$	—	—	—	$5\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3 \cdot 5$ aq.
Solution of $2\,NaNO_3$ $+ 3\,Na_2O \cdot 7\,MoO_3$ $+ KCl$	—	—	—	$5\,K_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3 \cdot 12$ aq. $\left.\begin{matrix}4\,K_2O\\Na_2O\end{matrix}\right\}\,2\,V_2O_5 \cdot 12\,MoO_3 \cdot 18$ aq.

Table E.

Action of MoO_3 on normal Vanadates and of V_2O_5 on normal and Paramolybdates[165].

The following substances were treated	with	Reaction products 1	2	3
$(NH_4)_2O \cdot V_2O_5$	MoO_3 at the temp. of boiling water (99°C.)	$3\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 11\,H_2O$	$(NH_4)_2O \cdot 2\,V_2O_5 \cdot 4\,H_2O$	—
$(NH_4)_2O \cdot V_2O_5$	MoO_3 on prolonged boiling	$5\,(NH_4)_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3 \cdot 10\,H_2O$	—	—
$K_2O \cdot V_2O_5$	do.	$5\,K_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3 \cdot 12\,H_2O$	—	—
$5\,(NH_4)_2O \cdot 12\,MoO_3$	V_2O_5 on prolonged boiling	$2\,(NH_4)_2O \cdot V_2O_5 \cdot 6\,MoO_3 \cdot 6\,H_2O$	$2\,(NH_4)_2O \cdot V_2O_5 \cdot 4\,MoO_3 \cdot 7\,H_2O$	—
$5\,K_2O \cdot 12\,MoO_3$	do.	$2\,K_2O \cdot V_2O_5 \cdot 6\,MoO_3 \cdot 6\,H_2O$	—	—
$K_2O \cdot MoO_3$	do.	$5\,K_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3 \cdot 12\,H_2O$	$3\,K_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 8\,H_2O$	$K_2O \cdot 2\,V_2O_5 \cdot 4\,H_2O$
$5\,R_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3$ $2\,R_2O \cdot V_2O_5 \cdot 6\,MoO_3$	$BaCl_2$ in the cold	$7\,BaO \cdot 3\,V_2O_5 \cdot 18\,MoO_3 \cdot 36\,H_2O$	—	—

Table F.

Action of MoO_3 on RH_2PO_4, R_2HPO_4 and R_3PO_4 (R=K, Na)[166].

Reacting substances	Reaction products		
$KH_2PO_4 + \frac{1}{2}$ Mol. MoO_3	$6\,K_2O \cdot 4\,P_2O_5 \cdot 9\,MoO_3 \cdot 40\,H_2O$	$4\,K_2O \cdot 3\,P_2O_5 \cdot MoO_3 \cdot 12\,H_2O$	—
$KH_2PO_4 + 1$ Mol. MoO_3	$7\,K_2O \cdot 5\,P_2O_5 \cdot 16\,MoO_3 \cdot 63\,H_2O$	$4\,K_2O \cdot 3\,P_2O_5 \cdot 9\,MoO_3 \cdot 33\,H_2O$	$K_2O \cdot P_2O_5 \cdot 2\,MoO_3 \cdot 13\,H_2O$
$KH_2PO_4 + 1\frac{1}{2}$ Mol. MoO_3	$3\,K_2O \cdot P_2O_5 \cdot 24\,MoO_3$	$3\,K_2O \cdot P_2O_5 \cdot 18\,MoO_3$	$4\,K_2O \cdot 3\,P_2O_5 \cdot 10\,MoO_3 \cdot 25\,H_2O$ and $\cdot 30\,H_2O$
$K_2HPO_4 + 1$ Mol. MoO_3	$5\,K_2O \cdot 2\,P_2O_5 \cdot 10\,MoO_3 \cdot 11\,H_2O$	$3\,K_2O \cdot P_2O_5 \cdot 5\,MoO_3 \cdot 7\,H_2O$	—
$K_2HPO_4 + 2$ Mol. MoO_3	$5\,K_2O \cdot 2\,P_2O_5 \cdot 10\,MoO_3 \cdot 20\,H_2O$	$2\,K_2O \cdot P_2O_5 \cdot 4\,MoO_3 \cdot 8\,H_2O$	$2\,K_2O \cdot P_2O_5 \cdot 5\,MoO_3 \cdot 6\,H_2O$
$K_3PO_4 + 2\frac{1}{2}$ Mol. MoO_3	$5\,K_2O \cdot 2\,P_2O_5 \cdot 10\,MoO_3 \cdot 20\,H_2O$	$3\,K_2O \cdot P_2O_5 \cdot 5\,MoO_3 \cdot 7\,H_2O$	$2\,K_2O \cdot P_2O_5 \cdot 5\,MoO_3 \cdot 6\,H_2O$
Na_3PO_4 saturated with MoO_3	$3\,Na_2O \cdot P_2O_5 \cdot 18\,MoO_3$	—	—
Na_2HPO_4 saturated with MoO_3	$5\,Na_2O \cdot 2\,P_2O_5 \cdot 48\,MoO_3 \cdot 100\,H_2O$	$3\,Na_2O \cdot P_2O_5 \cdot 18\,MoO_3 \cdot 25\,H_2O$	—

Table G.

Action of MoO_3 on $K_2O \cdot As_2O_5$ [167].

Reacting substances	Reaction products					
	1	2	3	4	5	6
$K_2O \cdot As_2O_5 + MoO_3$	$3\,K_2O \cdot As_2O_5 \cdot 6\,MoO_3$	$2\,K_2O \cdot As_2O_5 \cdot 4\,MoO_3$	KH_2AsO_4	H_3AsO_4	—	—
$K_2O \cdot As_2O_5 + 2\,MoO_3$	$5\,K_2O \cdot As_2O_5 \cdot 16\,MoO_3$	$2\,K_2O \cdot As_2O_5 \cdot 5\,MoO_3$	$K_2O \cdot AsO_5\ 2\,MoO_3 \cdot 5\,H_2O$	KH_2AsO_4	H_3AsO_4	—
$K_2O \cdot As_2O_5 + 2\,MoO_3$	$5\,K_2O \cdot As_2O_5 \cdot 16\,MoO_3$	$3\,K_2O \cdot As_2O_5 \cdot 4\,MoO_3$	$K_2O \cdot As_2O_5 \cdot 2\,MoO_3 \cdot 5\,H_2O$	KH_2AsO_4	H_3AsO_4	—
$K_2O \cdot As_2O_5 + 2\,MoO_3$	$1.75\,K_2O \cdot As_2O_5 \cdot 5.50\,MoO_3$	$5\,K_2O \cdot 2\,As_2O_5 \cdot 10\,MoO_3$	$2\,K_2O \cdot As_2O_5 \cdot 5\,MoO_3$	$K_2O \cdot As_2O_5\ 2\,MoO_3 \cdot 5\,H_2O$	KH_2AsO_4	H_3AsO_4
$K_2O \cdot As_2O_5 + 3\,MoO_3$	$1.58\,K_2O \cdot As_2O_5 \cdot 4.1\,MoO_3$	$K_2O \cdot As_2O_5 \cdot 2\,MoO_3 \cdot 5\,H_2O$	$K_2O \cdot As_2O_5 \cdot 6\,MoO_3 \cdot 5\,H_2O$	—	—	—
$K_2O \cdot As_2O_5 + 4\,MoO_3$	$5\,K_2O \cdot As_2O_5 \cdot 16\,MoO_3$	$K_2O \cdot As_2O_5 \cdot 2\,MoO_3 \cdot 5\,H_2O$	$K_2O \cdot As_2O_5 \cdot 6\,MoO_3 \cdot 5\,H_2O$	—	—	—

It is not difficult to show that the vanadomolybdates given in the Tables A, B, C, D, and E are genetically related to each other, as would be expected from the theory.

There must, of necessity, be a relation between vanadomolybdates in Tables A, B, and C, as these compounds are all obtained by the same method from different proportions of normal vanadates and MoO_3. The compounds shown in Table C must be related to those in A and B, as they are nothing more than transformation products of the latter. Hence the following genetic relationship between the vanadomolybdates :

(*a*)	$2\,R_2O \cdot V_2O_5 \cdot 6\,MoO_3$,
(*b*)	$5\,R_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3$,
(*c*)	$7\,R_2O \cdot 3\,V_2O_5 \cdot 18\,MoO_3$,
(*d*)	$R_2O \cdot V_2O_5 \cdot 3\,MoO_3$,
(*e*)	$2\,R_2O \cdot V_2O_5 \cdot 3\,MoO_3$,
(*f*)	$3\,R_2O \cdot 2\,V_2O_5 \cdot 6\,MoO_3$,
(*g*)	$2\,R_2O \cdot 2\,V_2O_5 \cdot 5\,MoO_3$,
(*h*)	$3\,R_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$,
(*i*)	$4\,R_2O \cdot 3\,V_2O_5 \cdot 5\,MoO_3$,
(*k*)	$5\,R_2O \cdot 4\,V_2O_5 \cdot 6\,MoO_3$,
(*l*)	$R_2O \cdot V_2O_5 \cdot MoO_3$.

Those shown in Table D, viz. :

(*a′*)	$3\,R_2O \cdot V_2O_5 \cdot 6\,MoO_3$,
(*b′*)	$5\,R_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3$,
(*c′*)	$2\,R_2O \cdot V_2O_5 \cdot 4\,MoO_3$,
(*d′*)	$2\,R_2O \cdot V_2O_5 \cdot 3\,MoO_3$,

must also be related, as they have been produced in an analogous fashion from normal vanadates and paramolybdates.

On the other hand, the vanadomolybdates (*b′*) and (*d′*) have a composition analogous to (*b*) and (*e*) in Tables A, B, and C, whereby the relationship of the various molybdates in the first four Tables enables them to form a definite class of compounds.

Table E includes the following :

(*a″*)	$2\,R_2O \cdot V_2O_5 \cdot 6\,MoO_3$,
(*b″*)	$5\,R_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3$,
(*c″*)	$7\,R_2O \cdot 3\,V_2O_5 \cdot 18\,MoO_3$,
(*d″*)	$2\,R_2O \cdot V_2O_5 \cdot 4\,MoO_3$,
(*e″*)	$3\,R_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3$.

From this Table (E) a relationship is shown between

1. a″, b″, c″ ;
2. a″, d″ and
3. b″, e″,

so that *a″*, *b″*, *c″*, *d″*, and *e″* must be analogously constituted.

As these substances are also shown in the Summary of Tables A, B, C, and D

$$\begin{aligned} a'' &= a, \\ b'' &= b' = b, \\ c'' &= c, \\ d'' &= c', \\ e'' &= h, \end{aligned}$$

there is a definite actual relationship between all the vanadomolybdates mentioned in Tables A, B, C, D, and E.

It is obvious that there can only be one theory which explains all these vanadomolybdates satisfactorily. The authors' hexite-pentite theory does this, and, what is more, it enables the existence of this relationship to be predicted. A study of the following structural formulæ of these vanadomolybdates leads to the surprising result that a large number of the theoretically constructed compounds of this group are actually in existence, and it is to be expected that the remaining vanadomolybdates—which are theoretically possible—will be discovered sooner or later.

The vanadomolybdates just mentioned clearly possess the following structural formulæ :

$$(2\,R_2O \cdot V_2O_5 \cdot 6\,MoO_3)_3 = \mathring{R}_{12}\left(\hat{V}\begin{matrix} \diagup \hat{Mo} \\ -\hat{Mo} \\ \diagdown \hat{Mo} \end{matrix}\right) \quad (a,\ a''),$$

$$7\,R_2O \cdot 3\,V_2O_5 \cdot 18\,MoO_3 = \mathring{R}_{14}\left(\hat{V}\begin{matrix} \diagup \hat{Mo} \\ -\hat{Mo} \\ \diagdown \hat{Mo} \end{matrix}\right) \quad (c,\ c''),$$

$$(5\,R_2O \cdot 2\,V_2O_5 \cdot 12\,MoO_3)_{1\cdot 5} = \mathring{R}_{15}\left(\hat{V}\begin{matrix} \diagup \hat{Mo} \\ -\hat{Mo} \\ \diagdown \hat{Mo} \end{matrix}\right) \quad (b,\ b',\ b''),$$

$$(3\,R_2O \cdot V_2O_5 \cdot 6\,MoO_3)_3 = \mathring{R}_{18}\left(\hat{V}\begin{matrix} \diagup \hat{Mo} \\ -\hat{Mo} \\ \diagdown \hat{Mo} \end{matrix}\right) \quad (a'),$$

$$\begin{aligned}
(R_2O \cdot V_2O_5 \cdot 3\,MoO_3)_6 &= \mathring{R}_{12}(\hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo}) \quad (d), \\
(2\,R_2O \cdot V_2O_5 \cdot 3\,MoO_3)_6 &= \mathring{R}_{24}(\hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo}) \quad (d',\ e), \\
(3\,R_2O \cdot 2\,V_2O_5 \cdot 6\,MoO_3)_3 &= \mathring{R}_{18}(\hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo}) \quad (f), \\
(2\,R_2O \cdot 2\,V_2O_5 \cdot 5\,MoO_3)_3 &= \mathring{R}_{12}(\overline{Mo} \cdot \hat{V} \cdot \overline{Mo} \cdot \hat{V} \cdot \overline{Mo}) \quad (g), \\
(3\,R_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3)_3 &= \mathring{R}_{18}(\hat{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \hat{Mo}) \quad (e'',\ h), \\
(4\,R_2O \cdot 3\,V_2O_5 \cdot 5\,MoO_3)_2 &= \mathring{R}_{16}(\overline{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \overline{Mo}) \quad (i), \\
(5\,R_2O \cdot 4\,V_2O_5 \cdot 6\,MoO_3)_2 &= \mathring{R}_{20}(\overline{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \overline{V}) \quad (k), \\
(R_2O \cdot V_2O_5 \cdot MoO_3)_6 &= \mathring{R}_{12}(\hat{V} \cdot \hat{Mo} \cdot \hat{V}) \quad (l), \\
(2\,R_2O \cdot V_2O_5 \cdot 4\,MoO_3)_3 &= \mathring{R}_{12}(\hat{Mo} \cdot \hat{V} \cdot \hat{Mo}) \quad (c',\ d'').
\end{aligned}$$

The objection may be raised to the conception of the α-vanadomolybdates as salts of complex acids: viz. the ratio of the acid components (V_2O_5 : MoO_3) must remain unchanged when the acids are treated with salts such as NaCl, KCl, etc., and the only substitution which can take place is by means of monovalent elements such as Na, K, etc. With the vanadomolybdates, however, this is not always the case. For instance, it may be seen from Table A, that the compound

$$(a') \qquad 5\,(NH_4)_2O \cdot 4\,V_2O_5 \cdot 6\,MoO_3 \cdot 14\,H_2O,$$

on treatment with KCl is converted into

$$(b') \qquad 3\,K_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 7\,H_2O.$$

The acid anhydride ratio in (a') is 2 : 3 and in (b') it is 1 : 2.

From the same Table it follows that

$$(c') \qquad 3\,K_2O \cdot (NH_4)_2O \cdot 3\,V_2O_5 \cdot 5\,MoO_3 \cdot 9\,H_2O,$$

on treatment with KCl is converted into

$$(d') \qquad 3\,K_2O \cdot 2\,V_2O_5 \cdot 4\,MoO_3 \cdot 7\,aq.$$

In (c') the ratio of $V_2O_5 : MoO_3 = 3 : 5$ and in (d') 1 : 2.

In this connection it should be borne in mind that—notwithstanding the undoubted existence of free complex acids of Mo and W, such as the silicotungstate $SiO_2 \cdot 12\,WO_3$, silicomolybdate $SiO_2 \cdot 12\,MoO_3$, phosphomolybdate $P_2O_5 \cdot 24\,MoO_3$, etc.—Friedheim and his associates endeavoured to regard molybdic and tungstic complexes as salts of related acids; they conceived the idea that they might be double salts and had hopes that this would suffice to explain the remarkable conversions they had observed. And yet these reactions are by no means so puzzling as may, at first sight, appear. Only the α-complexes of the aluminosilicates can be distinguished by a certain durability, e.g.

$$5.5\,R_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 \text{ (p. 39)},$$

in Lemberg's series. Whatever salts are allowed to act on the compounds in this series the aluminasilica ratio remains constant. In the α-components of the molybdic and tungstic complexes this is not always the case; they are, to some extent, unstable. The aluminosilicates are not all of equal stability. Of all the numerous types previously mentioned,

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si},$$

the kaolin type, is the most stable. It is well known that the action of various natural (geological) processes is to convert the various aluminosilicates into compounds of the kaolin type.

The great stability of compounds of the kaolin type is also shown by a series of fusion experiments by Doelter[168], who found that

1. Laumontite:

$$\mathring{C}a_3(\hat{Al} \cdot \hat{Si} \cdot \hat{Al}) \cdot 12\,H_2O,$$

at a sufficiently high temperature, loses silica and water, forming anorthite:

$$\mathring{C}a_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}).$$

2. On fusion, natrolite:

$$\mathring{N}a_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 12\,H_2O,$$

produces

$$\mathring{N}a_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

silica and water.

3. On fusion, scolecite:

$$\mathring{H}_{24}\mathring{C}a_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O,$$

yields

$$\mathring{C}a_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

silica and water.

If the vanadomolybdates and vanadotungstates are true analogues of the aluminosilicates, the most stable of the α-compounds must be

$$\hat{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \hat{Mo}, \text{ and}$$
$$\hat{W} \cdot \hat{V} \cdot \hat{V} \cdot \hat{W}.$$

This is actually the case, for Friedheim has shown that

$$(\alpha) \quad 6\,Na_2O \cdot 3\,V_2O_5 \cdot 6\,WO_3,$$

on boiling with WO_3, is converted into

$$(\beta) \quad 6\,Na_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3,$$

and on fusing β the α-compound

$$\hat{W} \cdot \hat{V} \cdot \hat{V} \cdot \hat{W},$$

remains behind.

On studying the puzzling transformations of the vanadomolybdates in the light of the hexite-pentite theory, it will be seen that the less stable α-compounds are converted into the highly stable

$$\hat{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \hat{Mo}.$$

The conversion of (a') into (b') and (c') into (b') may be represented as follows:

$$\underset{(a')}{\overline{V} \cdot \hat{Mo} \cdot \hat{V} \cdot \hat{Mo} \cdot \overline{V}} \longrightarrow \underset{(b')}{\hat{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \hat{Mo}},$$

$$\underset{(c')}{\overline{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \overline{Mo}} \longrightarrow \underset{(d')}{\hat{Mo} \cdot \hat{V} \cdot \hat{V} \cdot \hat{Mo}}.$$

No double decomposition can result from the action of KCl on (*a′*) or (*c′*), because these substances are unstable in solution, as may be found from their behaviour when attempts are made to crystallise them from such solution. The ratio $V_2O_5 : MoO_3$ in compounds of the type $\hat{\mathrm{Mo}} \,.\, \hat{\mathrm{V}} \,.\, \hat{\mathrm{V}} \,.\, \hat{\mathrm{Mo}}$ is not affected by reactions involving double decomposition.

The most stable type of compound may be represented by

$$\hat{\mathrm{V}}\!<\!\begin{array}{l}\hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\end{array}$$

deduced from the conversion of (*a″*) and (*b″*) into (*c″*) (Table E).

No less interesting is Table F, all the compounds of which, with the exception of

$$6\,K_2O \cdot 4\,P_2O_5 \cdot 9\,MoO_3 \cdot 4\,H_2O,$$

may be accurately represented by hexite-pentite formulæ, thus :

(*a*) $(2\,R_2O \cdot P_2O_5 \cdot 4\,MoO_3)_3 = \mathring{R}_{12}(\hat{\mathrm{Mo}} \cdot \hat{P} \cdot \hat{\mathrm{Mo}})$,

(*b*) $4\,R_2O \cdot 3\,P_2O_5 \cdot 10\,MoO_3 = \mathring{R}_8(\overline{\mathrm{Mo}} \cdot \hat{P} \cdot \overline{\mathrm{Mo}})$,

(*c*) $(R_2O \cdot P_2O_5 \cdot 2\,MoO_3)_6 = \mathring{R}_{12}(\hat{\mathrm{Mo}} \cdot \hat{P} \cdot \hat{P} \cdot \hat{\mathrm{Mo}})$,

(*d*) $(4\,R_2O \cdot 3\,P_2O_5 \cdot 9\,MoO_3)_2 = \mathring{R}_{16}(\hat{\mathrm{Mo}} \cdot \hat{P} \cdot \hat{\mathrm{Mo}} \cdot \hat{P} \cdot \hat{\mathrm{Mo}})$,

(*e*) $7\,R_2O \cdot 5\,P_2O_5 \cdot 16\,MoO_3 = \mathring{R}_{14}(\overline{\mathrm{Mo}} \cdot \overline{P} \cdot \hat{\mathrm{Mo}} \cdot \overline{P} \cdot \overline{\mathrm{Mo}})$,

(*f*) $(4\,R_2O \cdot 3\,P_2O_5 \cdot 4\,MoO_3)_3 = \mathring{R}_{24}(\hat{P} \cdot \hat{\mathrm{Mo}} \cdot \hat{P} \cdot \hat{\mathrm{Mo}} \cdot \hat{P})$,

(*g*) $(2\,R_2O \cdot P_2O_5 \cdot 5\,MoO_3)_3 = \mathring{R}_{12}\left(\hat{P}\!<\!\begin{array}{l}\overline{\mathrm{Mo}}\\ \overline{\mathrm{Mo}}\\ \overline{\mathrm{Mo}}\end{array}\right)$

(*g′*) $(5\,R_2O \cdot 2\,P_2O_5 \cdot 10\,MoO_3)_{1\cdot5} = \mathring{R}_{15}\left(\hat{P}\!<\!\begin{array}{l}\overline{\mathrm{Mo}}\\ \overline{\mathrm{Mo}}\\ \overline{\mathrm{Mo}}\end{array}\right)$

(*g″*) $(3\,R_2O \cdot P_2O_5 \cdot 5\,MoO_3)_3 = \mathring{R}_{18}\left(\hat{P}\!<\!\begin{array}{l}\overline{\mathrm{Mo}}\\ \overline{\mathrm{Mo}}\\ \overline{\mathrm{Mo}}\end{array}\right)$

(*h*) $(3\,R_2O \cdot P_2O_5 \cdot 18\,MoO_3) = \mathring{R}_6\left(\mathring{P}_2\!<\!\begin{array}{l}\hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\end{array}\right)$

(*i*) $2.5\,R_2O \cdot P_2O_5 \cdot 24\,MoO_3 = \mathring{R}_5\left(\begin{array}{l}\hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\end{array}\!>\!\dot{P}_2\!<\!\begin{array}{l}\hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\end{array}\right)$

(*i′*) $(3\,R_2O \cdot P_2O_5 \cdot 24\,MoO_3) = \mathring{R}_6\left(\begin{array}{l}\hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\end{array}\!>\!\mathring{P}_2\!<\!\begin{array}{l}\hat{\mathrm{Mo}}\\ \hat{\mathrm{Mo}}\end{array}\right)$

Altogether this series affords one of the most interesting confirmations of the hexite-pentite theory, and the advantages of grouping together these substances on the basis of their analogous mode of

formation are readily understood. Friedheim, on the contrary, suggests the following, particularly with regard to the compounds (*c*), (*d*), (*e*), and (*f*) :

" Only compound (*c*) of the previously unknown substance —the simplest of all those which contain phosphoric and molybdic acids—is of a simple nature . . . the other substances are undoubtedly mixtures."

Friedheim regards the compounds (*d*), (*e*), and (*f*) as " mixtures " simply because he could not otherwise explain their composition ! The Table is, therefore, only of value in so far as it shows a relationship between the α- and β-phosphomolybdate complexes !

Table G leads to the same conclusions as the others. The substances in it may clearly be expressed in the light of the hexite-pentite theory as follows :

$$(a)\quad (2\,R_2O \cdot As_2O_5 \cdot 4\,MoO_3)_3 = \mathring{R}_{12}(\hat{Mo} \cdot \hat{As} \cdot \hat{Mo}),$$

$$(a')\quad (3\,R_2O \cdot As_2O_5 \cdot 4\,MoO_3)_3 = \mathring{R}_{18}(\hat{Mo} \cdot \hat{As} \cdot \hat{Mo}),$$

$$(b)\quad (R_2O \cdot As_2O_5 \cdot 2\,MoO_3)_6 = \mathring{R}_{12}(\hat{Mo} \cdot \hat{As} \cdot \hat{As} \cdot \hat{Mo}),$$

$$(c)\quad (R_2O \cdot As_2O_5 \cdot 6\,MoO_3)_3 = \mathring{R}_6\left(\hat{As}\begin{array}{l}\diagup \hat{Mo}\\ - \hat{Mo}\\ \diagdown \hat{Mo}\end{array}\right)$$

$$(c')\quad (3\,R_2O \cdot As_2O_5 \cdot 6\,MoO_3)_3 = \mathring{R}_{18}\left(\hat{As}\begin{array}{l}\diagup \hat{Mo}\\ - \hat{Mo}\\ \diagdown \hat{Mo}\end{array}\right)$$

$$(d)\quad (2\,R_2O \cdot As_2O_5 \cdot 5\,MoO_3)_3 = \mathring{R}_{12}\left(\hat{As}\begin{array}{l}\diagup \overline{Mo}\\ - \overline{Mo}\\ \diagdown \overline{Mo}\end{array}\right)$$

$$(d')\quad (5\,R_2O \cdot 2\,As_2O_5 \cdot 10\,MoO_3)_{1\cdot 5} = \mathring{R}_{15}\left(\hat{As}\begin{array}{l}\diagup \overline{Mo}\\ - \overline{Mo}\\ \diagdown \overline{Mo}\end{array}\right)$$

$$(e)\quad 5\,R_2O \cdot As_2O_5 \cdot 16\,MoO_3 = \dot{R}_{10}\left(\mathring{As}_2\begin{array}{l}\diagup\\ -\\ \diagdown\end{array}\right)\begin{array}{l}\overline{Mo}\\ \hat{Mo}\\ \overline{Mo}\end{array}$$

Of further interest in connection with the hexite-pentite theory are the series of salts[170] produced by the action of V_2O_5 on potassium-, sodium- and ammonium-paratungstates :

1. $2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3$,
2. $4\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3$.

Of these, the first is immediately decomposed by acids—even in the cold—with separation of almost the whole of the tungstic acid. On evaporation with hydrochloric acid, the tungstic acid is precipitated

quantitatively in as complete a manner as in ordinary tungstic salts, though in this instance it is rendered impure by the co-precipitation of vanadic acid.

Compounds of the second series are not affected by acids.

Friedheim has endeavoured to show that the action of acids on the compounds in the first series brings about a separation of tungstic acid because they have, as one of their constituents, a paratungstate which behaves in the same manner. He therefore suggested the following equation:

$$(2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3)_3 = \underset{\text{(Paratungstate)}}{5\,R_2O \cdot 12\,WO_3} + R_2O \cdot 3\,V_2O_5.$$

The compounds of the second series he expressed as shown below, because the meta-tungstic acids behave in an analogous manner:

$$4\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3 = \underset{\text{(Metatungstate)}}{3\,(R_2O \cdot 4\,WO_3)} + R_2O \cdot 3\,V_2O_5.$$

Friedheim himself raised the following objection to his own conception of the molecular structure of the compounds of the first series[171]:

"The aqueous solution of the compound $2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3$ yields no precipitate on the addition of barium chloride or silver nitrate, but on evaporation with the first of these reagents the corresponding barium salt is formed; with silver nitrate a red solution, which changes after a time to a purple-reddish crystalline compound of the corresponding silver salt, is produced, and, if the solution is concentrated, the salt crystallises out in red needles."

It is scarcely likely that the compounds $2\,R_2O \cdot V_2O_5 \cdot 4\,WO_3$ contain the components shown by such a formula, as the latter does not indicate a substance which will form easily soluble barium and silver salts. In another research, Friedheim regards these compounds atomically, though even then it is scarcely possible to see, from Friedheim's structural formula (p. 21), that the bonds between the vanadium and the tungsten are different in the second group from what they are in the first. Yet this difference is at once observable in the following structural formulæ based on the authors' hexite-pentite theory:

$6\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3$ $\qquad$ $4\,R_2O \cdot 3\,V_2O_5 \cdot 12\,WO_3.$

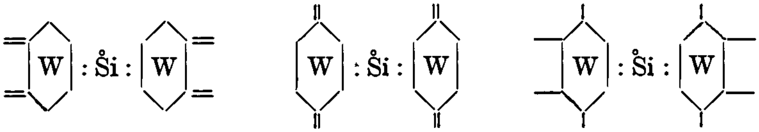
Valuable confirmation of the authors' theory is also found in the interesting researches by Marignac[172] on the silicotungstates. His formula ($SiO_2 \cdot 12\,WO_3$) at once suggests hexite.

For the compound

$$4\,H_2O \cdot SiO_2 \cdot 12\,WO_3,$$

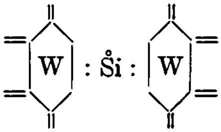
the hexite-pentite theory shows three isomers to be possible, viz.:

1. 2. 3.

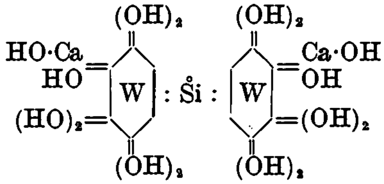


Marignac prepared two isomeric acids and two isomeric series of salts having the formula $4\,R_2O \cdot SiO_2 \cdot 12\,WO_3$.

The "water of constitution" in the free acids and in some of the salts may be demonstrated in a very accurate manner, as the acids $4\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 29\,H_2O$ lose 25 mol. H_2O at 100°, another 6 mol. between 150° and 220°, and are completely dehydrated at 350°. Hence, 8 mol. H_2O may be regarded as the "water of constitution" as shown in the structural formula:



The calcium salt, $2\,CaO \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 22\,H_2O$, loses 16 mol. H_2O at 100°, and it also contains 8 mol. H_2O as "water of constitution." This may be expressed thus:

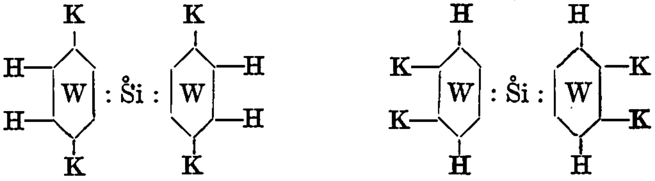


The potassium salt

$$2\,K_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 7\,H_2O$$

occurs in thick prisms and pearly hexagonal plates. Its dimorphism may be explained by the use of the following formula:

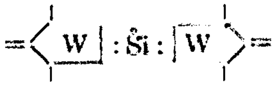
1. 2.



The silicotungstates may also be regarded as representing the β-complexes which, in molybdic and tungstic compounds, are so much

more stable than the α-complexes. The β-complexes usually yield free acids and the salts are not easily converted into compounds of other series, but will crystallise from their aqueous solution without any decomposition. The acid component ratio also remains unaffected by reactions involving a double decomposition.

Theoretically, the following compounds may exist :



$$4\ R_2O \cdot SiO_2 \cdot 10\ WO_3,$$

and Marignac also prepared compounds of this series.

The following formulæ for molybdic and tungstic β-complexes are derived from compounds mentioned in Dammer's "Handbook":

β-complexes

(*a*) $\dot{R}_2(Mo \cdot \dot{Al}_2 \cdot Mo)$,
(*b*) $\dot{R}_4(W \cdot \dot{B}_2 \cdot W)$,
(*c*) $\dot{R}_8(W \cdot \dot{Si} \cdot W)$,
(*d*) $\dot{R}_8(Mo \cdot \dot{Pt} \cdot Mo)$,
(*e*) $\dot{R}_8(W \cdot \dot{Pt} \cdot W)$.

(*a*) $\dot{R}_2(Mo \cdot \dot{Al}_2 \cdot Mo)$.

$K_2O \cdot Al_2O_3 \cdot 10\ MoO_3 \cdot 15\ H_2O$ (Parmentier[173]).

(*b*) $\dot{R}_4(W \cdot \dot{B}_2 \cdot W)$.

$2\ BaO \cdot B_2O_3 \cdot 10\ WO_3 \cdot 16\ H_2O$ (Klein[174]).

(*c*) $\dot{R}_8(W \cdot \dot{Si} \cdot W)$.

$4\ H_2O \cdot SiO_2 \cdot 10\ WO_3 \cdot 3\ H_2O$ (Marignac[175]).
$3\ (NH_4)_2O \cdot SiO_2 \cdot 10\ WO_3 \cdot 9\ H_2O$ „
$4\ (NH_4)_2O \cdot SiO_2 \cdot 10\ WO_3 \cdot 8\ H_2O$,
$2\ H_2O \cdot 2\ K_2O \cdot SiO_2 \cdot 10\ WO_3 \cdot 8\ H_2O$,
$4\ K_2O \cdot SiO_2 \cdot 10\ WO_3 \cdot 17\ H_2O$,
$4\ Ag_2O \cdot SiO_2 \cdot 10\ WO_3 \cdot 3\ H_2O$,
$4\ BaO \cdot SiO_2 \cdot 10\ WO_3 \cdot 22\ H_2O$.

(*d*) $\dot{R}_8(Mo \cdot \dot{Pt} \cdot Mo)$.

$4\ Na_2O \cdot PtO_2 \cdot 10\ MoO_3 \cdot 29\ H_2O$ (Gibbs[176]).

(*e*) $\dot{R}_8(W \cdot \dot{Pt} \cdot W)$.

$4\ (NH_4)_2O \cdot PtO_2 \cdot 10\ WO_3 \cdot 12\ H_2O$ (Gibbs[177]).
$4\ Na_2O \cdot PtO_2 \cdot 10\ WO_3 \cdot 25\ H_2O$,
$4\ K_2O \cdot PtO_2 \cdot 10\ WO_3 \cdot 12\ H_2O$.

(a) $R_4(Mo \cdot Al_2 \cdot Mo)$.
(b) $R_4(Mo \cdot Cr_2 \cdot Mo)$.
(c) $R_4(W \cdot B_2 \cdot W)$.
(d) $R_m(Mo \cdot Si \cdot Mo)$. (m = 4, 8)
(e) $R_8(W \cdot Si \cdot W)$.
(f) $R_2(Mo \cdot Zr \cdot Mo)$.
(g) $R_2(Mo \cdot Ti \cdot Mo)$.
(h) $R_m(W \cdot P_2 \cdot W)$. (m = 2, 4)
(i) $R_{10}(Mo \cdot I_2 \cdot Mo)$.

(a) $R_4(Mo \cdot Al_2 \cdot Mo)$.

$3\,(NH_4)_2O \cdot Al_2O_3 \cdot 12\,MoO_3 \cdot 20\,H_2O$ (Parmentier[178]).
$3\,K_2O \cdot Al_2O_3 \cdot 12\,MoO_3 \cdot 20\,H_2O$.
$3\,Na_2O \cdot Al_2O_3 \cdot 12\,MoO_3 \cdot 22\,H_2O$.

(b) $R_4(Mo \cdot Cr_2 \cdot Mo)$.

$3\,(NH_4)_2O \cdot Cr_2O_3 \cdot 12\,MoO_3 \cdot 20\,H_2O$ (Struve[179], Parmentier[180]).
$3\,K_2O \cdot Cr_2O_3 \cdot 12\,MoO_3 \cdot 20\,H_2O$ (S.).
$3\,Na_2O \cdot Cr_2O_3 \cdot 12\,MoO_3 \cdot 21\,H_2O$ (S.).

(c) $R_4(W \cdot B_2 \cdot W)$.

$2\,K_2O \cdot 2\,H_2O \cdot B_2O_3 \cdot 12\,WO_3 \cdot 10\,H_2O$ (Klein[181]).
$4\,K_2O \cdot B_2O_3 \cdot 12\,WO_3 \cdot 21\,H_2O$.
$K_2O \cdot 3\,BaO \cdot B_2O_3 \cdot 12\,WO_3 \cdot 28\,H_2O$.

(d) $R_m(Mo \cdot Si \cdot Mo)$; m = 4, 8.

$2\,H_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 24\,H_2O$ (Parmentier[182]).
$2\,H_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 30\,H_2O$ (Asch[183]).
$2\,(NH_4)_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 8\,H_2O$ (P.).
$2\,K_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 14\,H_2O$ (P.).
$2\,K_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 16\,H_2O$ (P.).
$1.5\,K_2O \cdot 0.5\,H_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 13.5\,H_2O$ (A.).
$2\,Na_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 21\,H_2O$
$1.5\,Na_2O \cdot 0.5\,H_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 16.5\,H_2O$.
$2\,Ag_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 12\,H_2O$.
$1.5\,Ag_2O \cdot 0.5\,H_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 10.5\,H_2O$.
$4\,Ag_2O \cdot SiO_2 \cdot 12\,MoO_3 \cdot 15\,H_2O$.
$2\,MgO \cdot SiO_2 \cdot 12\,MoO_3 \cdot 30\,H_2O$.
$2\,BaO \cdot SiO_2 \cdot 12\,MoO_3 \cdot 24\,H_2O$.
$2\,CaO \cdot SiO_2 \cdot 12\,MoO_3 \cdot 24\,H_2O$.

(e) $R_8(W \cdot Si \cdot W)$.

$4\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 22$ and $29\,H_2O$ (Marignac[184]).
$4\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 20\,H_2O$.
$4\,(NH_4)_2O\ SiO_2 \cdot 12\,WO_3 \cdot 16\,H_2O$.
$2\,(NH_4)_2O \,.\, 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 6\,H_2O$,

$4\,K_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 20\,H_2O$,
$2\,K_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 7\,H_2O$,
$2\,K_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 16\,H_2O$,
$3\,K_2O \cdot 5\,H_2O \cdot 2\,(SiO_2 \cdot 12\,WO_3) \cdot 25\,H_2O$,
$4\,Na_2O \cdot SiO_3 \cdot 12\,WO_3 \cdot 7\,H_2O$,
$2\,Na_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 10\,H_2O$,
$2\,Na_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 11\,H_2O$,
$2\,Na_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 18\,H_2O$,
$3\,(2\,Na_2O \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 13\,H_2O) \cdot 4\,Na_2NO_3$,
$Na_2O \cdot 3\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 14\,H_2O$,
$Na_2O \cdot 3\,BaO \cdot SiO_2 \cdot 12\,WO_3 \cdot 28\,H_2O$,
$2\,MgO \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 16\,H_2O$,
$5\,CaO \cdot 3\,H_2O \cdot 2\,(SiO_2 \cdot 12\,WO_3) \cdot 47\,H_2O$,
$2\,CaO \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 20\,H_2O$,
$2\,CaO \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 22\,H_2O$,
$4\,BaO \cdot SiO_2 \cdot 12\,WO_3 \cdot 27\,H_2O$,
$2\,BaO \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 14\,H_2O$,
$2\,BaO \cdot 2\,H_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot 22\,H_2O$.

(*f*) $\mathring{R}_2(\hat{Mo} \cdot \mathring{Zr} \cdot \hat{Mo})$.

$2\,(NH_4)_2O \cdot ZrO_2 \cdot 12\,MoO_3 \cdot 10\,H_2O$ (Pechard[185]),
$2\,K_2O \cdot ZrO_2 \cdot 12\,MoO_3 \cdot 18\,H_2O$.

(*g*) $\mathring{R}_2(\hat{Mo} \cdot \mathring{Ti} \cdot \hat{Mo})$.

$2\,K_2O \cdot TiO_2 \cdot 12\,MoO_3 \cdot 20\,H_2O$ (Pechard[186]),
$2\,(NH_4)_2O \cdot TiO_2 \cdot 12\,MO_3 \cdot 10\,H_2O$,
$2\,K_2O \cdot TiO_2 \cdot 12\,MO_3 \cdot 16\,H_2O$.

(*h*) $\mathring{R}_m(\hat{W} \cdot \mathring{P}_2 \cdot \hat{W})$; $m = 2.4$.

$P_2O_5 \cdot 12\,WO_3 \cdot 42\,H_2O$ (Pechard[187]),
$2\,(NH_4)_2O \cdot P_2O_5 \cdot 12\,WO_3 \cdot 5\,H_2O$,
$K_2O \cdot P_2O_5 \cdot 12\,WO_3 \cdot 9\,H_2O$,
$2\,Na_2O \cdot P_2O_5 \cdot 12\,WO_3 \cdot 18\,H_2O$,
$Li_2O \cdot P_2O_5 \cdot 12\,WO_3 \cdot 12\,H_2O$,
$Tl_2O \cdot P_2O_5 \cdot 12\,WO_3 \cdot 4\,H_2O$,
$Ag_2O \cdot P_2O_5 \cdot 12\,WO_3 \cdot 8\,H_2O$,
$2\,CuO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 11\,H_2O$,
$2\,ZnO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 7\,H_2O$,
$2\,PbO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 6\,H_2O$,
$2\,MgO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 10\,H_2O$,
$2\,CaO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 19\,H_2O$,
$2\,SrO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 17\,H_2O$,
$2\,BaO \cdot P_2O_5 \cdot 12\,WO_3 \cdot 15\,H_2O$.

(*i*) $\mathring{R}_{10}(\hat{Mo} \cdot \mathring{I}_2 \cdot \hat{Mo})$.

$5\,(NH_4)_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 12\,H_2O$ (Blomstrand[188]),
$9\,K_2O \cdot H_2O \cdot 2\,(I_2O_7 \cdot 12\,MoO_3) \cdot 24\,H_2O$,
$5\,Na_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 26\,H_2O$,
$5\,Na_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 34\,H_2O$,

$5\,Li_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 15\,H_2O,$
$5\,Li_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 18\,H_2O,$
$5\,CaO \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 26\,H_2O,$
$4\,CaO \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 21\,H_2O,$
$4\,SrO \cdot Na_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 20\,H_2O,$
$9\,BaO \cdot Na_2O \cdot 2\,(I_2O_7 \cdot 12\,MoO_3) \cdot 28\,H_2O,$
$2\,MnO \cdot 3\,Na_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot 32\,H_2O.$

$$\overset{\circ}{R}_2\left(\overset{\circ}{P}_2 \begin{matrix} \diagup \overline{Mo} \\ - \overline{Mo} \\ \diagdown \overline{\overline{Mo}} \end{matrix}\right)$$

$K_2O \cdot P_2O_5 \cdot 15\,MoO_3$ (Rammelsberg[189]).

(*a*) $$\overset{\circ}{R}_{10}\left(\overset{\circ}{Mn}_2 \begin{matrix} \diagup \overline{Mo} \\ - \hat{Mo} \\ \diagdown \overline{\overline{Mo}} \end{matrix}\right)$$

(*b*) $$\overset{\circ}{R}_6\left(\overset{\circ}{P}_2 \begin{matrix} \diagup \overline{Mo} \\ - \hat{Mo} \\ \diagdown \overline{\overline{Mo}} \end{matrix}\right)$$

(*c*) $$\overset{\circ}{R}_m\left(\overset{\circ}{P}_2 \begin{matrix} \diagup \overline{\overline{W}} \\ - \hat{W} \\ \diagdown \overline{\overline{W}} \end{matrix}\right); \qquad m = 1.2.$$

(*a*) $$\overset{\circ}{R}_{10}\left(\overset{\circ}{Mn}_2 \begin{matrix} \diagup \overline{Mo} \\ - \hat{Mo} \\ \diagdown \overline{\overline{Mo}} \end{matrix}\right)$$

$5\,(NH_4)_2O \cdot Mn_2O_3 \cdot 16\,MoO_3 \cdot 12\,H_2O$ (Struve[190]),
$5\,K_2O \cdot Mn_2O_3 \cdot 16\,MoO_3 \cdot 12\,H_2O.$

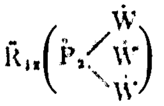
(*b*) $$\overset{\circ}{R}_6\left(\overset{\circ}{P}_2 \begin{matrix} \diagup \overline{Mo} \\ - \hat{Mo} \\ \diagdown \overline{\overline{Mo}} \end{matrix}\right)$$

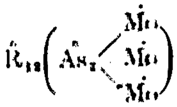
$3\,(NH_4)_2O \cdot P_2O_5 \cdot 16\,MoO_3 \cdot 14\,H_2O$ (Kehrmann[191]).

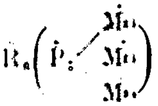
(*c*) $$\overset{\circ}{R}_m\left(\overset{\circ}{P}_2 \begin{matrix} \diagup \overline{\overline{W}} \\ - \hat{W} \\ \diagdown \overline{\overline{W}} \end{matrix}\right); \qquad m = 6.12.$$

$P_2O_5 \cdot 16\,WO_3 \cdot 69\,H_2O$ (Kehrmann[192]),
$3\,(NH_4)_2O \cdot P_2O_5 \cdot 16\,WO_3 \cdot 16\,H_2O$,,
$2\,BaO \cdot (NH_4)_2O \cdot P_2O_5 \cdot 16\,WO_3 \cdot x\,H_2O,$
$6\,(NH_4)_2O \cdot P_2O_5 \cdot 16\,WO_3 \cdot 2\,H_2O,$
$3\,K_2O \cdot P_2O_5 \cdot 16\,WO_3 \cdot 16\,H_2O,$
$2\,H_2O \cdot 4\,K_2O \cdot P_2O_5 \cdot 16\,WO_3 \cdot 19\,H_2O,$
$5\,H_2O \cdot CaO \cdot P_2O_5 \cdot 16\,WO_3 \cdot 3\,H_2O,$
$3\,BaO \cdot P_2O_5 \cdot 16\,WO_3 \cdot x\,H_2O.$

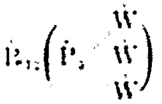
(*a*) $$\overset{\circ}{R}_6\left(\overset{\circ}{P}_2 \begin{matrix} \diagup \hat{Mo} \\ - \hat{Mo} \\ \diagdown \hat{Mo} \end{matrix}\right)$$

(b) 

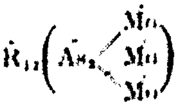
(c) 

(a) 

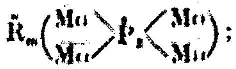
$(3 - x)\ Na_2O \cdot P_2O_5 \cdot 18\ MoO_3\ (25 + x)\ H_2O$ (Finkener[193]).

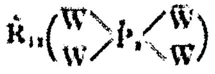
(b) 

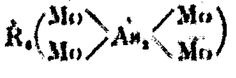
$6\ K_2O \cdot P_2O_5 \cdot 18\ WO_3 \cdot 23\ H_2O$ (Gibbs[194]).
$6\ K_2O \cdot P_2O_5 \cdot 18\ WO_3 \cdot 30\ H_2O$.
$K_2O \cdot 5\ H_2O \cdot P_2O_5 \cdot 18\ WO_3 \cdot 14\ H_2O$.

(c) 

$As_2O_5 \cdot 18\ MoO_3 \cdot 30$ and $28\ H_2O$ (Pufahl[195]).
$2\ (NH_4)_2O \cdot 4\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 13\ H_2O$ (Mac[196]).
$3\ K_2O \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 25\ H_2O$.
$K_2O \cdot 5\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 21\ H_2O$.
$3\ K_2O \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 21\ H_2O$.
$3\ Li_2O \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 31\ H_2O$,
$6\ Tl_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot x\ H_2O$.
$3\ Tl_2O \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 3\ H_2O$.
$6\ Ag_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 22\ H_2O$.
$7\ Ag_2O \cdot 5\ H_2O \cdot 2\ (As_2O_5 \cdot 18\ MoO_3) \cdot 22\ H_2O$.
$3\ CaO \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 29\ H_2O$.
$3\ SrO \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 29\ H_2O$.
$3\ MO \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 33\ H_2O$ (M = Mg, Cd, Mn, Co),
$3\ MO \cdot 3\ H_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot 34\ H_2O$ (M = Zn, Cu, Ni).

(a)  ; $m = 4, 6, 14$.

(b) 

(c) 

(a) $\mathring{R}_m\left(\begin{matrix}\overline{Mo}\\ \overline{Mo}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\overline{Mo}\\ \overline{Mo}\end{matrix}\right)$; m = 4, 6, 14.

$3\,H_2O \cdot P_2O_5 \cdot 20\,MoO_3 \cdot 21,\ 38\ \&\ 48\,H_2O$ (Debray[197]),
$2\,Ag_2O \cdot P_2O_5 \cdot 20\,MoO_3 \cdot 7\,H_2O$,
$3\,K_2O \cdot P_2O_5 \cdot 20\,MoO_3 \cdot 3\,H_2O$,
$7\,Ag_2O \cdot P_2O_5 \cdot 20\,MoO_3 \cdot 24\,H_2O$.

(b) $\mathring{R}_{12}\left(\begin{matrix}\overline{W}\\ \overline{W}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\overline{W}\\ \overline{W}\end{matrix}\right)$

$P_2O_5 \cdot 20\,WO_3 \cdot 62\,H_2O$ (Pechard[198]),
$P_2O_5 \cdot 20\,WO_3 \cdot 50\,H_2O$ (P.),
$6\,BaO \cdot P_2O_5 \cdot 20\,WO_3 \cdot 48\,H_2O$ (Gibbs[199]).

(c) $\mathring{R}_6\left(\begin{matrix}\overline{Mo}\\ \overline{Mo}\end{matrix}\right)\mathring{As}_2\left(\begin{matrix}\overline{Mo}\\ \overline{Mo}\end{matrix}\right)$

$As_2O_5 \cdot 20\,MoO_3 \cdot 27\,H_2O$ (Debray[200]),
$3\,K_2O \cdot As_2O_5 \cdot 20\,MoO_3 \cdot$

(a) $\mathring{R}_m\left(\begin{matrix}\overline{Mo}\\ \hat{Mo}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\overline{Mo}\\ \hat{Mo}\end{matrix}\right)$

(b) $\mathring{R}_m\left(\begin{matrix}\overline{W}\\ \hat{W}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\overline{W}\\ \hat{W}\end{matrix}\right)$

(a) $\mathring{R}_m\left(\begin{matrix}\overline{Mo}\\ \hat{Mo}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\overline{Mo}\\ \hat{Mo}\end{matrix}\right)$; m = 6, 14.

$3\,(NH_4)_2O \cdot P_2O_5 \cdot 22\,MoO_3 \cdot 9\,H_2O$ (Gibbs[201]),
$3\,(NH_4)_2O \cdot P_2O_5 \cdot 22\,MoO_3 \cdot 12\,H_2O$ (Rammelsberg[202]),
$3\,K_2O \cdot P_2O_5 \cdot 22\,MoO_3 \cdot$ (R.),
$5\,K_2O \cdot H_2O \cdot 2\,(P_2O_5 \cdot 22\,MoO_3) \cdot 21\,H_2O$ (R.),
$7\,Ag_2O \cdot P_2O_5 \cdot 22\,MoO_3 \cdot 14\,H_2O$ (G.).

(b) $\mathring{R}_m\left(\begin{matrix}\overline{W}\\ \hat{W}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\overline{W}\\ \hat{W}\end{matrix}\right)$; m = 4, 6, 8, 14.

$P_2O_5 \cdot 22\,WO_3 \cdot 7\,H_2O$ (Kehrmann[203]) and
$2\,K_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot 6\,H_2O$ (Gibbs[204]), (Freinkel),
$3\,(NH_4)_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot 21\,H_2O$ (G.),
$4\,BaO \cdot P_2O_5 \cdot 22\,WO_3 \cdot 41\,H_2O$ (G.),
$7\,K_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot x\,H_2O$ (K. and Fr.),
$7\,BaO \cdot P_2O_5 \cdot 22\,WO_3 \cdot 59.5\,H_2O$ (Sprenger, K. and Fr.),
$3\,BaO \cdot 4\,Ag_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot x\,H_2O$ (K.[205]).

(a) $\mathring{R}_m\left(\begin{matrix}\hat{Mo}\\ \hat{Mo}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\hat{Mo}\\ \hat{Mo}\end{matrix}\right)$

(b) $\mathring{R}_m\left(\begin{matrix}\hat{W}\\ \hat{W}\end{matrix}\right)\mathring{P}_2\left(\begin{matrix}\hat{W}\\ \hat{W}\end{matrix}\right)$

$$(a)\quad \mathring{R}_m\left(\begin{matrix}\hat{Mo}\\ \hat{Mo}\end{matrix}\right\rangle \mathring{P}_2 \left\langle\begin{matrix}\hat{Mo}\\ \hat{Mo}\end{matrix}\right)$$

$3\,H_2O \cdot P_2O_5 \cdot 24\,MoO_3 \cdot 27, 46\ \&\ 59\,H_2O$ (Gibbs[206]), Finkener[207]), Kehrmann[203]),

$3\,(NH_4)_2O \cdot P_2O_5 \cdot 24\,MoO_3 \cdot$ (Hundeshagen[209]),

$(9 - x)(NH_4)_2O \cdot x\,H_2O \cdot 3\,(P_2O_5 \cdot 24\,MoO_3)$ (Gibbs),

$5\,(NH_4)_2O \cdot H_2O \cdot P_2O_5 \cdot 24\,MoO_3 \cdot 16\,H_2O$,

$2\,K_2O \cdot H_2O \cdot P_2O_5 \cdot 24\,MoO_3 \cdot 3\,H_2O$,

$(3 - x)Na_2O \cdot P_2O_5 \cdot 24\,MoO_3 \cdot (58 + x)\,H_2O$.

$$(b)\quad \mathring{R}_m\left(\begin{matrix}\hat{W}\\ \hat{W}\end{matrix}\right\rangle \mathring{P}_2 \left\langle\begin{matrix}\hat{W}\\ \hat{W}\end{matrix}\right); \qquad m = 2, 4, 6.$$

$P_2O_5 \cdot 24\,WO_3 \cdot 40,\ 59$ and $60\,H_2O$ (Pechard[210]), (Gibbs[211]), (Sprenger[212]),

$3\,(NH_4)_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 20\,H_2O$ (Gibbs),

$3\,K_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 11$ or $17\,H_2O$ (Gibbs),

$3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 22\,H_2O$ (Brandhorst and Kraut[213]), (Kehrmann[214]),

$Na_2O \cdot 2\,BaO \cdot P_2O_5 \cdot 24\,WO_3 \cdot 46\,H_2O$,

$2\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 27\,H_2O$,

$3\,Ag_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 58\,H_2O$,

$Ag_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 60\,H_2O$,

$3\,CaO \cdot P_2O_5 \cdot 24\,WO_3 \cdot 58\,H_2O$,

$3\,BaO \cdot P_2O_5 \cdot 24\,WO_3 \cdot 58, 46\,H_2O$,

$2\,BaO \cdot P_2O_5 \cdot 24\,WO_3 \cdot 59\,H_2O$,

$BaO \cdot P_2O_5 \cdot 24\,WO_3 \cdot 60\,H_2O$,

etc. etc.

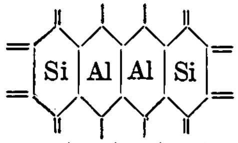
XI

The Constitution of Clays

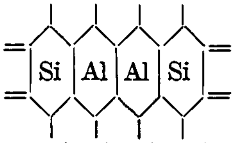
The hexite-pentite theory shows the possible existence of a large number of aluminosilicic acids in the form of hydrates and anhydrides. Thus, if

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si},$$

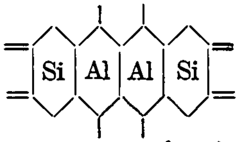
is taken as the type, the following hydrates are possible :



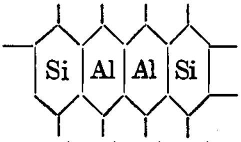
$H_{20}^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
1.



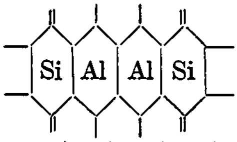
$H_{16}^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
2.



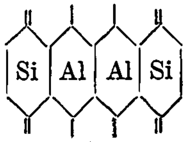
$H_{12}^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
3.



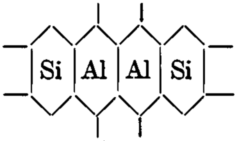
$H_{12}^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
4.



$H_{16}^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
5.

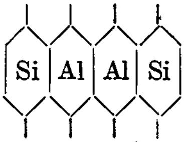


$H_{12}^{\circ}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$
6.



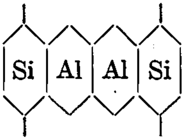
$H_8^{o}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

7.



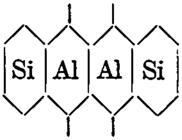
$H_8^{o}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

8.



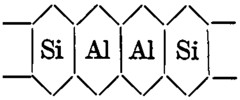
$H_4^{o}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

9



$H_4^{o}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

10.



$H_4^{o}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

11.

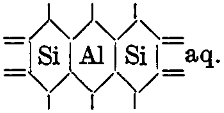
Of the above hydrates or aluminosilicic acids, Nos. 3, 4, and 6, also 2 and 5, also 9, 10, and 11 are isomeric. If all the contained water is completely separated, the anhydride

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}$$

is formed.

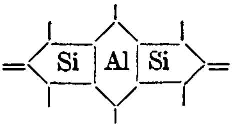
The above hydro-alumino-silicates may also contain a variable proportion of "water of crystallisation," the number of hydrates being thereby increased.

Analogous hydrates—with or without water of crystallisation—may, naturally, be regarded as of other types; by the complete loss of their contained water, these hydrates may form a corresponding series of anhydrides. The following hydrates and the corresponding anhydrides thus become theoretically possible:

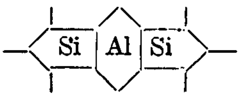


1.

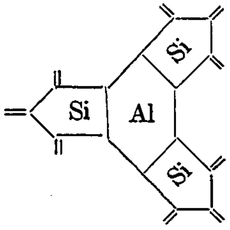
2.



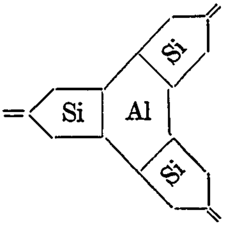
3.

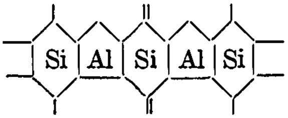


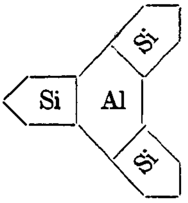
4.

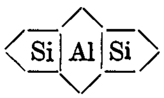


aq









etc. etc.

8. 9.

These substances have seldom, if ever, been prepared synthetically, though their occurrence in Nature is well known under such widely different names as "Minerals of the Allophane Group," "Clays," and "Kaolins." They have been formed out of the most diverse materials, such as micas, felspars, chlorites, etc., by removal of the base, hydration and subsequent removal of the water under definite conditions.* These acids are seldom found in a chemically pure state, but usually contain small proportions of the original base. Hence some of them may, rightly, be termed *strongly acid salts.*

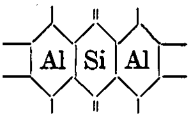
Their formulæ have seldom been calculated from analyses, as these materials have usually been regarded as "mixtures." The formulæ calculations of some minerals of the allophane group[215] (see *Appendix*) showed that these substances are hydro-aluminosilicates (with a small lime content) of the type

$$\hat{Al} \cdot \hat{Si} \cdot \hat{Al} \text{ and } \hat{Al} \cdot \overline{Si} \cdot \hat{Al}.$$

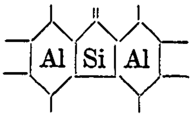
From the analyses, the following formulæ were calculated :

1. $0.5\ CaO \cdot 6\ Al_2O_3 \cdot 6\ SiO_2 \cdot 32\ H_2O$,
2. $0.5\ CaO \cdot 6\ Al_2O_3 \cdot 6\ SiO_2 \cdot 38\ H_2O$,
3. $0.75\ CaO \cdot 6\ Al_2O_3 \cdot 6\ SiO_2 \cdot 32\ H_2O$,
4. $0.25\ CaO \cdot 6\ Al_2O_3 \cdot 5\ SiO_2 \cdot 32\ H_2O$,
5. $0.75\ CaO \cdot 6\ Al_2O_3 \cdot 6\ SiO_2 \cdot 42\ H_2O$.

Part of the water present is in the form of "water of crystallisation" and part as "water of constitution." It is not possible to state *a priori* how much water exists in either or both these forms, but the maximum proportion of "water of constitution" which is possible may be predicted on theoretical grounds, as in the two following structural formulæ :



Maximum of H_2O-Mols.
(6)



Maximum of H_2O-Mols.
(5)

* The various theories as to the origins of clays are described in the translator's "British Clays"[706] and "Natural History of Clay"[731].—A. B. S.

The determination of water present after heating these substances to a high temperature should, therefore, be of value.

Equally interesting is the calculation of the formulæ of a number of washed clays from the analyses published in C. Bischof's "Collected Analyses of Materials used in Clayworking," published in 1901 (see *Appendix*—'Clays,' Section B).

These analyses agree with the theory that a number of hydro-aluminosilicates may exist in which the alumina-silica ratio varies within extremely wide limits, so that the hydro-aluminosilicates themselves may be of the most widely varying nature. The analyses indicate the following substances :

(*a*) $\dot{Si} \cdot \dot{R} \cdot \dot{Si}$.

(*b*) $Si \cdot \dot{R} \cdot Si$.

(*c*) $R \begin{cases} \dot{Si} \\ Si \\ Si \end{cases}$

(*d*) $R \begin{cases} \dot{Si} \\ Si \\ Si \end{cases}$

(*e*) $\dot{Si} \cdot R \cdot R \cdot Si$.

(*f*) $Si \cdot R \cdot R \cdot Si$.

(*g*) $Si \cdot R \cdot \dot{Si} \cdot R \cdot Si$.

(*h*) $Si \cdot \dot{R} \cdot Si \cdot R \cdot Si$.

(*i*) $\dot{Si} \cdot R \cdot Si \cdot R \cdot Si$.

More accurate calculations of the formulæ from analyses by the same investigator (see *Appendix*—'Clays,' Section C) gave the following :

I. $0.5\,CaO \cdot 5.5\,H_2O \cdot 3\,R_2O_3 \cdot 15\,SiO_2 = H^{*}_{11}Ca^{*}_{\cdot1}\left(R \begin{matrix} Si \\ Si \\ Si \end{matrix}\right)$

II. $0.25\,K_2O \cdot 19.75\,H_2O\,(5\,R_2O_3 \cdot 12\,SiO_2)_3 = [H^{*}_{10}Si \cdot R \cdot R \cdot Si]_3$ (+ some K.).

III. $0.5\,R_2O \cdot 15.5\,H_2O \cdot 6\,R_2O_3 \cdot 16\,SiO_2 = H_{11}R^{*}_{\cdot1}(Si \cdot R \cdot Si \cdot R \cdot Si) \cdot 5\,H_2O$,

IV. $0.5\,CaO \cdot 15.5\,H_2O \cdot 6\,R_2O_3 \cdot 16\,SiO_2 = H^{*}_{11}Ca^{*}_{\cdot1}(Si \cdot R \cdot Si \cdot R \cdot Si) \cdot 5\,H_2O$.

VIII. $0.5\,K_2O \cdot 8.5\,H_2O \cdot 5\,Al_2O_3 \cdot 16\,SiO_2 = H_{11}K^{*}(Si \cdot Al \cdot \dot{Si} \cdot Al \cdot Si)$.

IX. $0.5\,K_2O \cdot 9.5\,H_2O \cdot 6\,R_2O_3 \cdot 15\,SiO_2 = H^{*}_{19}K^{*}(Si \cdot R \cdot Si \cdot \dot{R} \cdot Si)$.

XII. $0.25\,K_2O \cdot 9.75\,H_2O \cdot 6\,R_2O_3 \cdot 16\,SiO_2 = H^{*}_{10}(Si \cdot R \cdot \dot{Si} \cdot R \cdot Si)$ (+ some K.).

XIII. $12\,H_2O \cdot 6\,R_2O_3 \cdot 18\,SiO_2 = H^{*}_{12}(\dot{Si} \cdot R \cdot \dot{Si} \cdot \dot{R} \cdot \dot{Si})$.

XV. $10\,H_2O \cdot 5\,R_2O_3 \cdot 12\,SiO_2 = H^{*}_{18}(\dot{Si} \cdot R \cdot R \cdot \dot{Si}) \cdot H_2O$.

These compounds contain only very small proportions of base and may, therefore, be regarded as hydro-aluminosilicates. The constitutional formulæ * suggested are only tentative so far as their "water of constitution" is concerned; it is not impossible that in some of them a part of what is, above, included under the term "water of constitution" may, in reality, be in the form of "water of crystallisation." The only means of ascertaining this is to make determinations of the water left after heating the substances to various high temperatures.

Further formulæ calculated from the analyses of the foregoing and other clays will show whether the other theoretically possible hydro-aluminosilicates are known to occur in Nature or to have been prepared artificially.

According to the authors' hexite-pentite theory, clays must have the properties of *acids*. The following equation represents the action of sodium carbonate:

$$\dot{Si} \cdot \dot{Al} \cdot \dot{Al} \cdot \dot{Si} + 6\,Na_2CO_3 = Na_{12}(\bar{Si} \cdot \bar{Al} \cdot \bar{Al} \cdot \bar{Si}) + 6\,CO_2.$$

According to Vernadsky[216] haloid salts (KI, KBr, etc.) decompose clays at moderate and high temperatures, with separation of haloid salts.

The *acidity* of clays is also shown by their mode of formation in Nature. They are formed by the decomposition of aluminosilicates under the same conditions as hydrates and anhydrides are formed by the decomposition of their salts. Thus, in Nature, the decomposition of simple silicates by the action of water and carbonic acid produces opals, and a similar decomposition of aluminosilicates produces clays.

The necessary consequence of the hexite-pentite theory—that clays are single chemical compounds and not mixtures—is by no means new. So far as certain Alsatian fireclays are concerned, this conclusion was reached by C. Mène in a prize essay published in 1863, in which he made the following noteworthy statement:

"The clays used for the manufacture of firebricks are compounds of definite chemical composition and are decomposition products of rocks of equally definite chemical composition."

This work of Mène's appears to have been overlooked, and many modern scientists generally—though erroneously—regard clays as mixtures of quartz, felspar and the so-called "clay substance." This highly mistaken view of the chemical nature of clays is due to a peculiarity possessed by them, easily explicable in the light of the hexite-pentite theory, but otherwise only by assuming the existence of a definite "clay substance." This peculiarity consists in the fact that, like all other aluminosilicates, *clays are decomposed at high*

* The distribution of the OH-groups in these formulæ is described at greater length in the later sections—on Ultramarine, Portland Cements, and Porcelain Cements.

temperatures and by some concentrated acids, forming compounds of the most stable type possible, such as the following :

1. $\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}}$,
2. $\overline{\mathrm{Si}} \cdot \dot{\mathrm{Al}} \cdot \hat{\mathrm{Al}} \cdot \overline{\mathrm{Si}}$, and
3. $\hat{\mathrm{Si}} \cdot \overline{\mathrm{Al}} \cdot \overline{\mathrm{Al}} \cdot \hat{\mathrm{Si}}$.

If, for instance, a clay of the type

$$\hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{Al}} \cdot \hat{\mathrm{Si}} = 6\,\mathrm{Al_2O_3} \cdot 18\,\mathrm{SiO_2}$$

is treated with concentrated sulphuric acid, it loses silica or silica and alumina, according to the temperature and duration of treatment, forming a compound of one of the three types just mentioned.

This is also shown by the researches of C. Bischof[218] (see *Appendix*, 'Clays'—D), who was one of the first to study the action of sulphuric acid on the following clays :

1. $\mathrm{m\,RO} \cdot 5\,\mathrm{R_2O_3} \cdot 17\,\mathrm{SiO_2} \cdot \mathrm{aq.}$,
2. $\mathrm{m\,RO} \cdot 5\,\mathrm{R_2O_3} \cdot 16\,\mathrm{SiO_2} \cdot \mathrm{aq.}$,
3. $\mathrm{m\,RO} \cdot 3\,\mathrm{R_2O_3} \cdot 12\,\mathrm{SiO_2} \cdot \mathrm{aq.}$,
4. $\mathrm{m\,RO} \cdot 5\,\mathrm{R_2O_3} \cdot 17\,\mathrm{SiO_2} \cdot \mathrm{aq.}$,
5. $\mathrm{m\,RO} \cdot 3\,\mathrm{R_2O_3} \cdot 15\,\mathrm{SiO_2} \cdot \mathrm{aq.}$,
6. $\mathrm{m\,RO} \cdot 5\,\mathrm{R_2O_3} \cdot 18\,\mathrm{SiO_2} \cdot \mathrm{aq.}$,
7. $\mathrm{m\,RO} \cdot 6\,\mathrm{R_2O_3} \cdot 12\,\mathrm{SiO_2} \cdot \mathrm{aq.}$

The action of sulphuric acid may be represented as follows :

1. $\hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \longrightarrow \overline{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}}$,
2. $\overline{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}} \longrightarrow \overline{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}}$,
3. $\hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \longrightarrow \overline{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{R}} \cdot \overline{\mathrm{Si}}$,
4. $\hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \longrightarrow \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}}$,
5. $\hat{\mathrm{R}} \begin{cases} \overline{\mathrm{Si}} \\ \overline{\mathrm{Si}} \\ \overline{\mathrm{Si}} \end{cases} \longrightarrow \overline{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{R}} \cdot \overline{\mathrm{Si}}$,
6. $\hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \longrightarrow \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}}$,
7. $\hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \longrightarrow \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{R}} \cdot \overline{\mathrm{Si}}$.

The above examples—which may be increased indefinitely—show conclusively that clays are really converted into the highly stable compounds stated. The alumina-silica ratio is approximately 1 : 2—which cannot be a mere coincidence—and the supposition that clays contain a " clay substance " separable by acids—though erroneous—is a very natural one.

Mellor and Holdcroft[708] consider that clays are decomposed by sulphuric acid in another manner, viz. with separation of silica and the formation of aluminium sulphate. This view is highly improbable, as an almost constant ratio of $\mathrm{Al_2O_3}$ and $\mathrm{SiO_2}$ has been found in the solution by numerous investigators, and this constancy is the foundation of the theory of the so-called " clay substance."

Forchhammer[219] appears to have been the first to express any doubt as to the unitary nature of clays. He supposed that in sulphuric acid he had found a valuable "solvent" for clays and regarded that portion which entered into solution as "clay" and the remainder as "undecomposed felspar." From time to time, doubts have been expressed* as to the value of the so-called "rational analysis," but the remarkable resistance of clays to strong acids is the chief reason why Forchhammer's conception of "clay substance" is still maintained, though modern chemists represent it by a different formula.

Forchhammer's theory of clays is now of merely historical interest and must be abandoned as inconsistent with the facts.

[With it, the rational analysis must also be abandoned, at any rate as far as the usual interpretation of its results are concerned.†]

There is, at the present time, no fact known which is not compatible with the unitary chemical nature of clays as opposed to the view that they are mixtures.

[This statement must be taken to refer to "purified" clays, for many materials are commonly termed "clay" which obviously contain other constituents. Thus "boulder clay" contains limestone and other stones, loams contain sand which may be removed by simple washing, and many "clays" contain rock-debris of a nature clearly distinct from clay. Unfortunately, some of these obviously "non-clay" materials are in so fine a state that they cannot be perfectly separated by elutriation or similar mechanical processes. It does, however, appear to be true that, quite apart from the hexite-pentite theory, the essential constituents of clays are definite alumino-silicates.]

Minerals of the allophane group are characterised by the ease with which they are decomposed by acids. Other hydro-aluminosilicates, including several clays, are only readily decomposed by dilute acids after they have been heated very strongly. The reason for this difference in the behaviour of substances which, according to the authors' hexite-pentite theory, are analogous, can only be explained in the following manner:

"Disdynamised" and "Dynamised" Compounds

It has been shown, in connection with the tungstates (p. 95), that the presence of a base weakens the bonds in the ring-radicles of complexes. Thus, tungstovanadates with a small content of base are not decomposed by acids, but in those richer in base a precipitate of tungstic acid readily forms when they are treated with acids. The bonds between the ring-radicles of complex substances may also be weakened in other ways, such as by an increase in the proportion of "water of constitution" or "water of crystallisation" or by subjecting the substance to a high temperature.

Compounds in which the chemical relationship between the ring-

* Seger investigated this subject and recommended it—under the title of "rational analysis"—for relatively pure clays, but found it unsatisfactory for the clays used for the manufacture of bricks, tiles, cement, etc. Brongniart and Malaguti[220] did not question the "undoubted advantages of rational analysis," but saw in the results obtained an uncertainty "which compels us to draw conclusions with very great care."

† Additions and comments by the translator which cannot conveniently be inserted as footnotes are printed in smaller type.

radicles is weakened by these means so that the substance becomes readily decomposable by dilute acids, are said to be " disdynamised " in order to distinguish them from the "dynamised" substances which resist the action of dilute acids.

The reason why minerals of the allophane group are readily decomposed by dilute acids is now clear : in them the relationship between the silicon- and aluminium-hexites has been weakened by the presence of a high proportion of combined water.

Clays usually contain only " water of constitution " ; on heating to vitrification they are disdynamised and then behave like the analogous minerals of the allophane group.

[The vitrification point of a clay is that temperature to which it must be heated in order that sufficient fusion may occur for most of the pores in the clay to be filled with fused matter, yet without the material losing its original shape to any appreciable extent. In most clays there appears to be no single temperature at which this occurs to the exclusion of others ; the material becomes vitrified gradually throughout a range of temperature which sometimes extends over 400° C., though some clays vitrify completely in a very few moments after the fusion of some of their constituents has commenced. This property of vitrification is extremely important in the technical application of clays; further information about it will be found in the translator's "British Clays, Shales, and Sands."[705] It is, however, possible that this *range* of vitrification is due to difficulties in maintaining a perfectly constant temperature for a sufficiently long time. If, as Doelter has suggested, the vitrification point is definable as that at which fusion is first observed to commence, and if, further, in accordance with A. Stock's investigations, which showed that the vitrification point and the true melting point of a silicate are identical and that vitrification occurs on heating perfectly pure crystalline chemical compounds, then it should be possible to produce a completely vitrified mass by maintaining the material for a sufficiently long time at the lowest temperature at which fusion can be observed to occur. The cost and difficulty of doing this with reasonably large masses of clay are very great, as the conductivity of the material is so low, but so far as the translator's own experiments go, and in so far as he has been able to find other similar experimental evidence, there are good reasons for believing that the apparent *range* of vitrification or of fusion is merely a result of the extraordinarily low conductivity of clay and of the high temperature at which fusion occurs. Could clays be fused at temperatures as easily observed as those used in studying the melting points of many organic compounds, there is great probability that pure clays would be found to have a sharply defined melting point. As it is, the only means of effecting vitrification or fusion within a reasonably short time consists in raising the temperature considerably above that which would be necessary if time were no consideration. In other words, the term "range of vitrification" indicates a practical experience even if it may lead to the erroneous assumption that clays differ from other definite chemical compounds in not having a sharp, well-defined melting point.]

In order to understand the nature of the state of disdynamisation produced when clays are heated to vitrification, it is necessary to assume that oxygen has two kinds of valency—primary and secondary—and that the bonding of the ring-radicles is due to both the primary and the secondary valencies of oxygen. If the proportion of base or combined water in the compound is increased, the secondary valencies are set free either partially or completely according to the proportion of base or water. On increasing the temperature, the bound secondary affinities are also partially or completely liberated, according to the temperature to which the substance is heated.

It is conceivable that as soon as the secondary valencies are set free, a *looser* bond must exist between the ring-radicles of the complexes concerned.

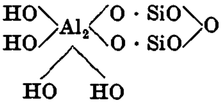
At the vitrification temperature, the nascent secondary oxygen valencies of the disdynamised clay molecules at once begin to be liberated, and this may readily lead to the formation of polymerisation products. If the temperature increases, the liberation also increases, and when it is complete the whole of the material is reduced to a molten state. It is clear that as the temperature rises, the polymerisation increases, and this is, necessarily, followed by an increase in density. When the mass is completely fused, the point of maximum density will have been reached.

[Some highly interesting investigations by R. Rieke[707] on the temperature at which certain clays lose their "combined water" are worth special attention. This investigator followed Le Chatelier's observation that if a sample of kaolin is slowly heated there is a point at which the temperature ceases to rise for some minutes, after which it again rises steadily. If the temperature and duration of the heating are plotted as ordinates and abscissæ, the graph produced will show a marked flattening about 500° C. Rieke examined 10 kaolins, 8 plastic fireclays, 6 non-refractory clays (red-burning), and 2 shales, and in each case he found that a marked absorption of heat occurred and was shown by the flattening of the graph at a temperature of 500° to 580° C. The purer the clays, the more noticeable is this break in the rise of temperature.

In clays containing much free quartz the absorption of heat is obscured by the reactions which the quartz undergoes at the temperatures mentioned, and the more complex graphs of the impure clays may be further affected by the reactions of other compounds present.

Rieke also found that the loss of water corresponded to the flattening of the heating curve; a notable evolution of water commences at 450° C., and almost the whole of the water is removed at a temperature of 550° to 600° C., though for its complete expulsion prolonged heating at a higher temperature appears to be necessary. The rate of evolution of water is not regular, and diminishes rapidly when most of the water has been removed. It is increased by reducing the pressure of the air surrounding the clay.

Mellor and Holdcroft[708] have independently confirmed Rieke's observations with respect to china clay, and have concluded that the "china clay molecule" must have its OH-groups placed symmetrically. They accept a slight modification of Groth's formula,* viz.:



More recently, Mellor has examined crystalline kaolinite in a similar manner and finds its behaviour is identical with that of the purest Cornwall china clay.

Unlike the authors of the present volume, Mellor and Holdcroft conclude that the "clay molecule" is decomposed into its constituent oxides—alumina and silica—at 500° C.,† and consider that the formation of sillimanite at higher temperatures (1200° C.) is a confirmation of this in accordance with the equation:

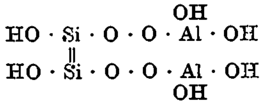
$$Al_2O_3 + SiO_2 = Al_2SiO_5.$$

They agree that polymerisation of the alumina occurs (with evolution of heat at 800° C.), but have published no formula for the polymerisation-product. In other words, they regard the latter as though it were the simple non-polymerised substance when (according to them) it reacts at 1200° C. with the silica to form sillimanite.

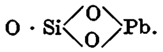
* The views of the authors of the present volume as to the distribution of the OH-groups are described at greater length in the later sections—on Ultramarine, Portland Cements, and Porcelain Cements—and the following formulæ are also criticised on p. 116.

† See p. 113.

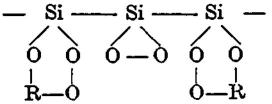
W. Pukall[710] has suggested the formula:



and in opposition to all other writers indicates a double bond between the silicon atoms. From what has been stated on previous pages, however, the bond between the silicon atoms must contain oxygen. The view that a direct connection exists between the silicon atoms is also held by Simmonds[721], who studied the action of hydrogen at high temperatures on lead meta-silicate, to which is usually assigned the formula:



He reached the conclusion that both oxygen atoms cannot occupy similar positions, and suggested the following formula for this silicate:



Simmonds thus suggests that the silicon atoms are connected directly with each other and not through the medium of oxygen atoms. Manchot and Keiser[722] were unable to confirm Simmonds' observation on lead silicates, and rightly argue that silicon compounds in which the silicon atoms are directly connected with each other *must evolve hydrogen* when treated with hydrofluoric acid and then with alkali, yet this reaction never occurs with the silicates now under consideration. Manchot[723] uses this argument in criticising Pukall's formula, and adds that such a double bond would imply that kaolinic acid would be more easily decomposed by alkalies than by other silicates with a single bond, whereas kaolinic acid is very resistant to alkalies.

Singer[724] has also criticised Pukall's formula unfavourably and has pointed out that a double silicon bond, like a double carbon bond, is a source of weakness in a compound rather than one of strength.

The re-combination of water with the dehydrated kaolin is also of interest as throwing further light on the constitution of the molecule. Mellor and Holdcroft (*l.c.*) found that even in an autoclave at 300° C. under a pressure of 200 atmospheres the dehydrated china clay only absorbed 2·5% of water. Rieke found that a Bohemian kaolin, which had been heated at 500° C. until all the water had been removed, could only be made to re-combine with 1·1% of water. The very small proportion of re-combination which occurs is a further proof of the remarkably high stability of the anhydride Ŝi · Âl · Âl · Ŝi, as pointed out by the authors of the present volume.]

Burning Clays

[" Burning " is a term used to indicate the heating of articles made of clay under industrial conditions in kilns or ovens in order to give them the characteristics desired in pottery, bricks, tiles, etc. It differs from simple heating (or calcination) in that the clays have been formed into articles of the desired shape and in that the heating must usually be prolonged and the rise in temperature must be very slow so as to avoid the splitting and cracking of the goods.

This explanation is necessary, as the shape of the articles and the speed of the heating are important determinants of the character of the heated material. In " burning," clays are never supposed to be heated to such an extent as to cause them to fuse sufficiently for loss of shape to occur. When this happens they are " over-burned."]

So long as clays are regarded as mixtures of quartz, undecomposed felspar and " clay substance," no satisfactory explanation of what occurs during the burning is possible. The great difference in the effect of dilute acids on raw and burned clays makes it obvious that some

definite chemical reactions must occur during the burning. The nature of these reactions has, hitherto, been inexplicable. From a "mixture," all kinds of simple and double salts might be formed, and these cannot be adequately examined. Yet a correct understanding of the burning process is not only of academic value, but of great practical importance. Hence, the hexite-pentite theory should be of great assistance in indicating the chemical reactions which take place on burning.

These reactions may be stated in terms of the Disdynamisation Theory (p. 108) as follows:

1. On heating a clay to vitrification, part of or all the "water of constitution" is evolved. Secondary valencies of some of the oxygen atoms are set free, but *the clay itself retains its unitary chemical nature and is not decomposed into its constituent oxides.*

2. If the temperature exceeds that necessary for vitrification, the free valencies liberate themselves and form polymerisation products, the clays eventually fusing either partially or completely. Hence fused clays must possess properties chemically different from those which have been merely vitrified. The density of fired clays must also be higher than that of vitrified clays.

3. Vitrified clays must be more easily attacked by acids than unvitrified ones.

[This "consequence" is erroneous, as explained below.]

[In this connection, the extensive use of vitrified (stoneware) clays in the manufacture of acids and in the construction of appliances (stills, etc.) in which hot acids are used is important. General experience appears, at first sight, to be in direct contradiction to the authors' statement in this paragraph, as vessels made of clay which has been vitrified are usually found to be amongst the most powerful resistants to all acids except hydrofluoric.

It is probable, however, that polymerisation products and the presence of these and of fused material of a highly resistant nature may be the cause of this anomaly, the term "vitrified" used in the text being understood to refer to clays which have only been heated to the lowest temperature at which vitrification can possibly occur, and not to a temperature at which polymerisation products are formed. If this is the case and the disdynamic action is stopped on polymerisation or partial fusion, the apparent anomaly is destroyed and the authors' theory becomes conformable to general experience.]

The observations of Mellor and Holdcroft[208] and others show that clay which has been heated to a certain temperature is (in accordance with the theory) more readily attacked by acids than that which has not been heated. It is also a well-known fact that on further heating at a still higher temperature a material is produced which is resistant to acids (in contradiction to the theory). Such polymerisation as occurs will, however, make the heated clay resistant to acids. In this connection it must be remembered that the polymerisation brought about by disdynamisation is itself a dynamisation and so increases the resistance of the material to chemical influences. The rise of temperature can, in fact, only have a complete disdynamic action when no polymerisation occurs. This fact was overlooked by the authors until it was pointed out to them by A. B. Searle, and this oversight is the cause of the erroneous conclusion reached in Consequence 3 of the theory.

4. The so-called "decomposition" (p. 107) by concentrated acids is merely a disdynamisation.

The observation of R. Rieke that, on burning clays, their temperature does not rise steadily, but remains constant for a long time, notwithstanding the increased temperature of the kiln, may be explained in terms of the new theory if the constant temperature occurs at the sintering point of the clay.

The statement made by Desch that clays heated to 700° can easily add calcium silicate, calcium aluminate, or calcium hydrate may be explained by the new theory of burning stated below.

The behaviour of the silicate molecule towards acids also depends on the number of aluminium hydroxyl groups in the molecule. This must always be borne in mind when studying this subject, and is therefore dealt with exhaustively in the following chapter.

There can be no doubt that the rise in temperature exerts a disdynamising action on clays, and that in consequence of this action molecular changes are produced in addition to such polymerisation as may occur. This is particularly the case with kaolin, as will be seen on reading the following chapter. If the theory is extended in this manner it will be found to be in complete agreement with the observed facts.

It is not then necessary, as Mellor and Holdcroft suggest, to assume that, on heating, clays are decomposed into free silica and alumina and that a re-combination of these oxides occurs on further heating.

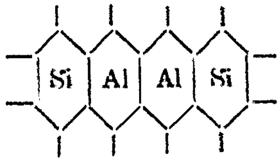
The investigations of Richter, Bischof, Jochum, Rieke and others have shown that the fusing point of clays is greatly influenced by the impurities, such as quartz, alkalies, etc., present. A theory of burning to be satisfactory must take this into consideration.

This consideration of the burning process may be allowed to suffice as an explanation of the decomposition of slightly heated clay by acids and its greater resistance after heating at a higher temperature. At the same time, this theory of burning leads to no conclusions with regard to certain properties of kaolin which are described in the following chapter. It may, therefore, be necessary to modify the application of the Disdynamisation theory to burning, as further facts are observed.

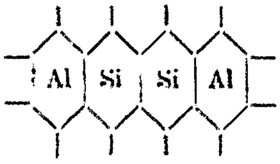
The Isomerism and Polymerisation of Kaolin

From the formula $6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$ (kaolin) two isomeric substances may be formed. *

* If a rule is made to name the central core first and then the side chains, the acid A may be termed *di-h-alumino-di-h-silicic acid*, and the acid S *di-h-silico-di-h-aluminic acid*. Hence the salts of the *A*-acid and all silicates with a central aluminium core may be termed *aluminosilicates*, whilst the salts of the *S*-acid and all compounds with a central silicon core may be termed *silicoaluminates*.

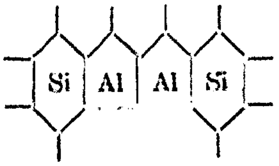


A.



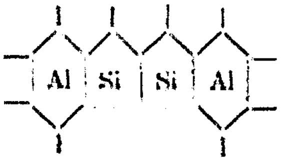
S.

A number of derivatives of these two acids in which pentites replace hexites are theoretically possible:



A′.

and



S′.

A″.

and

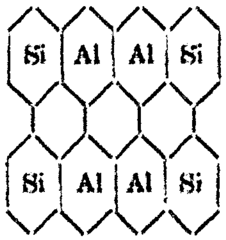
S″.

In accordance with the foregoing nomenclature these acids may be termed:

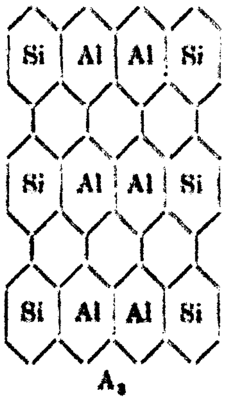
A′ . . . . . . *Di-p-alumino-di-h-silicic acid.*
A″ . . . . . . *Di-h-alumino-di-p-silicic acid.*
S′ . . . . . . *Di-p-silico-di-h-aluminic acid.*
S″ . . . . . . *Di-h-silico-di-p-aluminic acid.*

The acids with central aluminium rings may be shortly termed *a-kaolinic acids*, and those with central silicon rings as *s-kaolinic acids.*

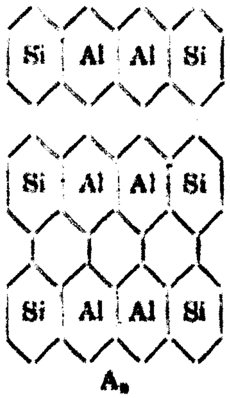
Two, three or more molecules of the acids A, A′, or A″ and of the acids S, S′ or S″ may lose certain molecules of water and then unite to form polymerisation products. Thus, the following compounds are possible:



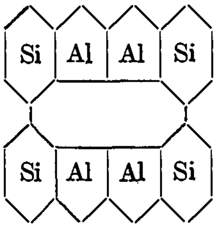
A_1



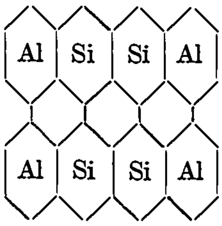
A_2



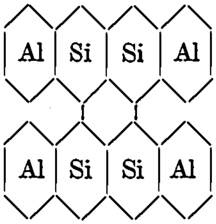
A_3



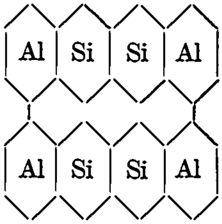
A'_2



S_2



S'_2



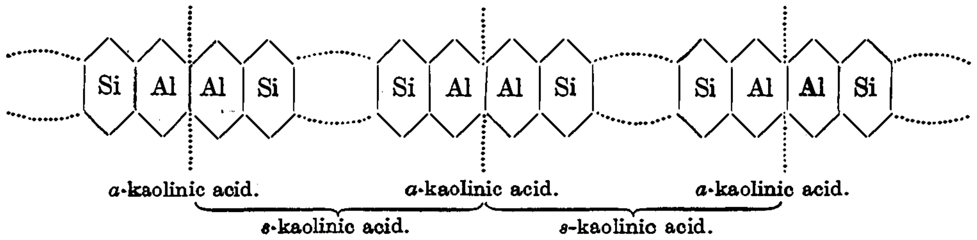
S''_2

etc. etc.

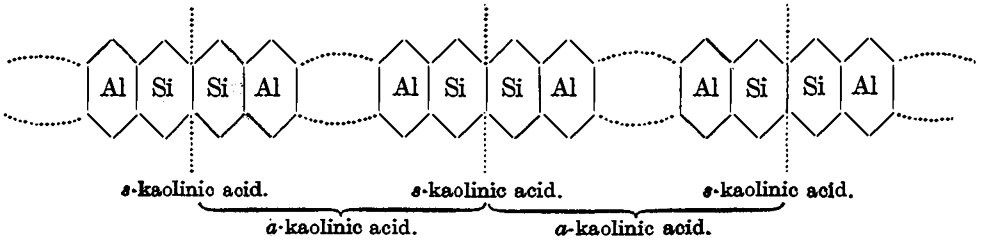
On polymerisation, separation of water can only occur in two analogous rings, as in the centre of the S'_2 or the side rings of the S''_2 compounds.

Between the *a*- and *s*-kaolinic acids and their salts there must be a genetic relationship, as they can be converted into each other. This transformation may be represented as follows :

I. Conversion of the *a*-kaolinic acid into *s*-kaolinic acid :



II. Conversion of the *s*-kaolinic acid into *a*-kaolinic acid



In an analogous manner the *polymerised* a-kaolinic acids may be converted into polymerised s-kaolinic acids and *vice versâ.*

In the chapter on Ultramarines and Porcelain cements two kinds of hydroxyl groups in kaolinic acids are described : termed a- and s-hydroxyls, respectively. The former—the hydroxyls of the aluminium rings—are acidophillic, and the latter—the hydroxyls of the silicon rings—are basophillic. The kaolinic acids—both simple and polymerised—appear to contain more s-hydroxyls and less a-hydroxyls ; the s-kaolinic acids, on the contrary (both simple and polymerised), contain more a-hydroxyls and less s-hydroxyls.

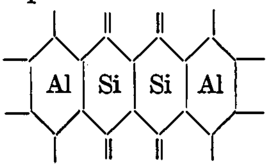
These variations in the number of a- and s-hydroxyls of the a- and s-kaolinic acids must result in these acids having a different relationship to other acids and a different solubility in acids. The more a-hydroxyls a-kaolinic acid contains, *the more soluble must it be in acids, or in other words, the s-kaolinic acids must usually be more soluble in acids than the analogous isomers or a-kaolinic acids.*

As the degree of polymerisation must diminish with a-hydroxyls, it follows that, *cæteris paribus, the polymerised kaolinic acids must be less soluble in acids than the non-polymerised ones.* From the theory it follows that the anhydrides of the a-kaolinic acids have the lowest degree of solubility in acids, and therefore the greatest resistance to acids. If the plasticity of clays is a function of the water of constitution (see p. 65) it follows that :

1. The a-kaolinic acids can generally have a higher degree of plasticity than the s-kaolinic acids, as the former contain more water of constitution.

2. The polymerised kaolinic acids have, *cæteris paribus,* a lower plasticity than the non-polymerised ones.

The a- and s-kaolinic acids must also differ from each other in physical characters, such as density, resistance to reagents, etc., as well as in chemical structure. There is another interesting consequence of the new theory as applied to kaolinic acids :—In the salts of the kaolinic acids, such a compound as



$8\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2,$

Normal sodium s-kaolinate.

must have the sodium united to the silicon ring (i.e. s-sodium) more strongly than the a-sodium attached to the aluminium ring ; i.e. in this compound half the sodium must be more strongly united than the remainder. It is also probable, on *a priori* grounds, that this sodium salt will behave differently towards different acids ; the stronger acids can remove the whole of the sodium (both a- and s-sodium), but the weaker acids can only remove the a-sodium.

The Hexite-Pentite Theory and the Facts

The available experimental material is in entire agreement with the theory developed in the preceding pages. In this connection the work of (*a*) W. Pukall[710] and (*b*) Mellor and Holdcroft[708] on kaolinisation is of special value.

I

The Study of Kaolinisation by W. Pukall[710]

W. Pukall has endeavoured to prepare kaolin synthetically, and from a mixture of 18·75 of quartz, 24·38 of aluminium hydrate, 150 of caustic soda and 75 c.c. water heated in a silver crucible until the mass became stiff, he obtained a product which, on washing, yielded a white, crystalline substance which melted at Seger cone 7 (about 1270°), i.e. the temperature at which salt glazed ware is glazed.

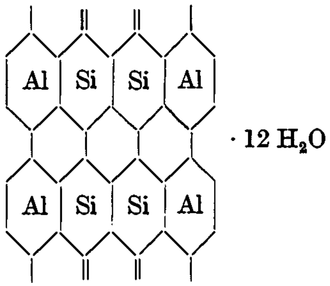
Zettlitz kaolin or English china clay when melted with ten times its weight of common salt at 950° C. evolved water and hydrochloric acid and combined with sufficient soda (28%) to be comparable to $Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2$. Both these kaolins are converted into a crystalline substance.

Multiplying the formula just mentoned by 6, the following compound:

$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 12\,H_2O,$$

is formed ; it may be the salt of either an *a*- or an *s*-kaolinic acid.

From Pukall's investigations it appears highly probable that the salt he obtained is a polymerised sodium *s*-kaolinic acid of the following formula :



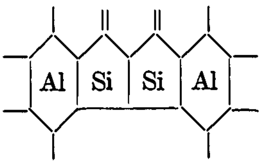
$$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 12\,H_2O.$$

As the ratio $Al_2O_3 : SiO_2$ in the salt obtained by Pukall is the same as that in kaolin, he endeavoured to remove the Na_2O and to obtain the free acid, i.e. the "kaolin." For this purpose he used two methods : by treatment with (*a*) carbonic acid and (*b*) hydrochloric acid. The results of these two experiments, whilst in agreement with the H.P. theory, were quite different : the carbonic acid, as a *weak* acid, only removes the *a*-sodium and converts the Si-hexites into pentites ; the

hydrochloric acid, as a *strong* acid, removes the whole of the *a*-sodium and half the *s*-sodium, as may be seen from the following :

a. The Behaviour of Pukall's Sodium *s*-Kaolinate towards Carbonic Acid

The sodium di-s-kaolinate ($6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2\ 12\ H_2O$) of the above-mentioned structure was heated in a Soxhlet's apparatus for 264 hours with carbonic acid in order to remove the soda, and by this means Pukall obtained a substance corresponding to the formula



$\cdot 12H_2O$

$$2\ Na_2O \cdot 4\ H_2O \cdot 10\ SiO_2 \cdot 6\ Al_2O_3 \cdot 12\ H_2O.$$

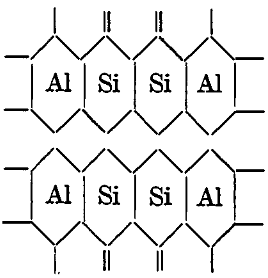
The analyses made confirm this formula :

	Na_2O	H_2O	Al_2O_3	SiO_2
Calculated	7.63	17.76	37.68	36.94
Found	7.10	19.95	37.49	36.82

The carbonic acid converts the Si-hexite into Si-pentite as already described. The feebly acid carbonic acid can only remove the acidophillic aluminium rings, and not the strongly basophillic Si-rings.

b. The Behaviour of Pukall's Sodium *s*-Kaolinate towards Hydrochloric Acid

Pukall also endeavoured to remove the Na_2O in the sodium salt above mentioned by means of a stronger acid, for which purpose he selected hydrochloric acid. The sodium salt dissolves in this acid and is obtained, on treatment with ammonia, in the form of a voluminous white precipitate corresponding to



	($R_2O\ 4\ H_2O$		$12\ SiO_2$	$6\ Al_2O_3)_2$	$32\ H_2O$.
	$0.5\ Na_2O$	$0.5\ (NH_4)_2O$	$12\ SiO_2$	$6\ Al_2O_3$	$20\ H_2O$.
Calculated	1.77	1.48	41.16	34.99	20.58
Found	2.15	1.26	42.07	36.33	20.00

Pukall did not determine the proportion of Na_2O and $(NH_4)_2O$ and suggested the following formula :

	$3\,H_2O$	Al_2O_3	$2\,SiO_2$
Calculated	19.57	36.91	43.47
Found	20.00	36.93	42.07

The hydrochloric acid, being a strong acid, removes some base from the sodium salt, yet a small proportion of the base still remains. It is probable that the hydrochloric acid removes half the *s*-sodium ; the remainder being replaced by NH_4.

It has already been shown that the chemical and physical properties of any *s*-kaolinic acid must differ from those of any *a*-kaolinic acid, and an acid *s*-kaolinate must differ still more widely from "kaolin" (*a*-kaolinic acid). As a matter of fact, Pukall has proved that kaolin is different from the kaolinate inasmuch as the former only loses its water on heating to redness, but the latter parts with half its water at temperatures below 350° C. and the remainder on heating to redness. Other properties of these two substances also confirm the view that they require different structural formulæ. Kaolin, for example, is very plastic on account of the many OH-groups it contains. The number of OH-groups in the acid kaolinate is much less and part of them are replaced by basic groups. Hence, it is not surprising that Pukall should find this salt to be less plastic than kaolin.* When Pukall's salt is mixed with quartz and felspar it forms a very lean mixture, and on heating this to 1370° a beautiful, white, translucent porcelain is produced. If the same salt is mixed with free silica and alumina the mixture is not plastic, though kaolin, when similarly treated, retains its plasticity. Moreover, this mixture does not produce a true porcelain on burning.

Pukall has also prepared the above-mentioned sodium salt of *s*-kaolinic acid by another method. On boiling and then fusing kaolin with caustic soda and a little hydrated alumina, and then washing the product, a white crystalline mass is obtained which Pukall has shown to be the above-mentioned sodium *s*-kaolinate. This method is of great theoretical importance, as it shows a definite genetic relationship must exist between the *a*-kaolinic acid and the *s*-kaolinic acid ; one being converted into the other under certain conditions. This agrees with the results obtained by Mellor and Holdcroft and discussed in the next section.

Pukall has, further, made the interesting discovery that if silica and alumina are heated with an excess of a very strong alkali solution the compound produced $(xAl_2O_3 \cdot 2xSiO_2)$ always has the same molecular ratio of alumina and silica, no matter whether the silica and alumina are free or in a combined state.

* For notes on the relationship between plasticity and chemical constitution, see page 133.

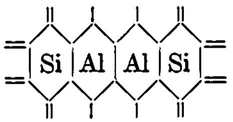
II

The Study of Kaolin by Mellor and Holdcroft[703]

Mellor and Holdcroft have studied the structure of kaolin by means of the purest china clay obtainable, this kaolin having a composition approximating very closely indeed to the formula :

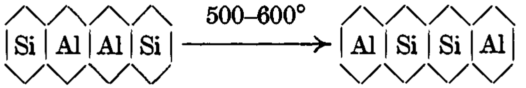
$$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O.$$

The result of their investigations leads to the conclusion that in all probability china clay is an *a*-kaolinic acid with a structure represented by the formula * :



$$2\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 10\,H_2O.$$

This *a*-kaolinic acid is converted on heating to 500–600° C. into a derivative of *s*-kaolinic acid, as shown in the following diagram :



At a higher temperature (800–900° C.) the *s*-kaolinic anhydride is polymerised with a liberation of heat, and at a temperature of 1100–1200° the polymeric anhydride of the *s*-acid is converted into a polymeric anhydride of the *a*-kaolinic acid with absorption of heat.

In this way the genetic relationship between the *s*- and the *a*-kaolinic acid previously discovered by Pukall is confirmed.

The changes just mentioned are based on the following considerations :—

1. The heating curve plotted by Mellor and Holdcroft for pure kaolin shows, at temperatures above 500° C., a reduction in the rate at which the temperature rises, and this is doubtless due to the occurrence of an endothermic or heat-absorbing reaction. At 900° C. a feeble exothermic reaction occurs, and between 1000° and 1200° another strong endothermic reaction takes place. These three "critical temperatures" are due to † :—

(*a*) The conversion of the *a*-kaolinic acid into the anhydride of *s*-kaolinic acid.

(*b*) The polymerisation of the anhydride of the *s*-kaolinic acid.

(*c*) The conversion of the polymerised anhydride of the *s*-kaolinic acid into a polymerised anhydride of the *a*-kaolinic acid.

* Mellor and Holdcroft's formula is given on p. 110.

† Mellor and Holdcroft's interpretation of these results is given on p. 122.

2. If this conversion of the *a*-kaolinic acid into an anhydride of the *s*-kaolinic acid really does take place at a temperature of 500–600° C. as stated above, it follows that the product formed by heating kaolin to this temperature must be more readily soluble than the original kaolin. This interesting consequence of the H.P. theory has been independently and experimentally confirmed by Mellor and Holdcroft, who found that the dehydrated kaolin is more active than the kaolin from which it was prepared, and its solubility in acetic, hydrochloric and nitric acids is greater than that of the unburned kaolin.

It is probable that the anhydride of the *s*-kaolinic acid formed at 600° C. becomes partially hydrated when under the influence of these acids, and the acidophilic OH groups (the *a*-OH groups) thus formed, and twice as numerous as the OH groups in the *a*-kaolinic acid molecule, will make the product more closely related to acids and will simultaneously increase its solubility in acids.

3. A glance at the structural formulæ of the simple and polymerised *a*- or *s*-kaolinic acids shows that :—

(*a*) The polymerised anhydrides of the *a*- and *s*-kaolinic acids must have a greater resistance to acids than those which are not polymerised.

(*b*) The greatest resistance to acids must be shown by the anhydrides of the polymerised *a*-kaolinic acids, and

(*c*) The *s*-kaolinic acids and their anhydrides must split off alumina more readily than silica, when treated with acids.

These consequences of the H.P. theory are all confirmed by Mellor and Holdcroft's experiments ; the following being of special interest :—

Samples of china clay, which had been maintained at various temperatures, were shaken mechanically, with hydrochloric acid of specific gravity 1·165 diluted with an equal volume of water, for two hours, and the proportions of alumina and silica dissolved were then determined. Pure hydrated alumina and pure hydrated silica were similarly treated. The results are shown in the following Table :—

	Kaolin			Alumina		Silica	
Temperature.	Loss on Heating. %	Soluble Matter		Loss on Heating %	Soluble Matter %	Loss on Heating %	Soluble Matter %
		SiO_2 %	Al_2O_3 %				
100°	12.64	0.08	0.12	—	—	16.00	2.60
600°	1.37	0.18	0.16	2.45	42.96	—	1.36
700°	0.62	0.12	0.98	2.41	29.40	—	1.36
800°	0.56	0.12	0.68	1.58	7.84	1.24	1.12
900°	0.23	0.12	0.20	1.65	5.92	0.43	0.76
1000°	0.25	0.06	0.16	0.05	0.00	0.05 (at 1200°)	0.68

It will be observed that the solubility of the alumina in the china clay after heating to 600° is only slightly higher than that in the clay heated to 100°. It appears as if the conversion of the *a*-kaolinic acid into *s*-kaolinic acid commences at this temperature. At 700° there is a notable increase in the proportion of soluble alumina; at higher temperatures the solubility of the alumina appears to diminish so that at 800° C. it is only 0·68; at 900° it is still lower, and, at 1000°, the solubility of both silica and alumina is very small. The solubility of the alumina in china clay does not agree entirely with the conclusions previously expressed (see Section I, p. 120) in which it was stated that the conversion of the *a*-kaolinic acid into the anhydride of the *s*-kaolinic acid occurs at 500–600° C., but the above Table clearly offers a general confirmation of the theory inasmuch as it shows an increased solubility in hydrochloric acid as the temperature to which china clay is heated is increased.

4. The specific gravity of the *s*-kaolinic acids must, clearly, differ from that of the *a*-kaolinic acids and the investigations of Mellor and Holdcroft have shown that this is the case, the specific gravity diminishing as the conversion of the *a*- into the *s*-kaolinic acid takes place. The Table below shows that at 600° the specific gravity of the clay is distinctly lower than at 110°.

At high temperatures the polymerisation which occurs and the formation of the polymerised anhydride of *a*-kaolinic acid must necessarily result in a series of increases in the specific gravity of the material. Mellor and Holdcroft have (without recognising the true nature of the compounds with which they were dealing) determined the specific gravity of the various *a*- and *s*-kaolinic acid derivatives, as shown in the following Table:

Temperature.	Specific Gravity.
110°	2.615
600°	2.473
700°	2.469
800°	2.497
900°	2.560
1000°	2.734

Hence the various consequences of the H.P. theory as applied to the kaolinic acids are in complete agreement with the facts.

Mellor and Holdcroft have endeavoured to explain the three critical temperatures (500–600°, 800–900°, and 1100–1200°), mentioned above, which are recognisable on heating kaolin, and the abnormal behaviour of dehydrated kaolin towards acids, on the assumption that (*a*) between 500° and 600° the substance loses all its water and is decomposed into free silica and alumina, (*b*) polymerisation of the alumina occurs at 800–900°, and (*c*) the free silica and alumina re-com-

bine at 1100–1200°. This explanation of Mellor and Holdcroft's is highly improbable, and is contradicted by their experimental results. Thus, the Table showing the solubility of kaolin, alumina, and silica which have been heated to various temperatures (*supra*) shows that at 700° only 0·98 per cent. of the alumina presumably set free from the china clay is dissolved, whilst 20·4 per cent. of the hydrated alumina is dissolved under similar conditions. To suggest that this low solubility is due to the alumina being in the nascent state is to make the whole experiment quite inexplicable, as alumina definitely known to be in this state has a still higher solubility. In any case, such a difference in solubility as Mellor and Holdcroft suppose is quite incomprehensible, and their assumption that the alumina from the clay is more readily converted into an insoluble modification than that existing when hydrated alumina is heated is untenable, as the difference in solubility is far too large. Moreover, such an assumption is unnecessary, because, as already explained, the hexite-pentite theory gives a much simpler interpretation which is in closer agreement with the facts.

The hygroscopicity of china clay, alumina and silica which had been heated to various temperatures has also been determined by Mellor and Holdcroft. The values obtained appear to be in opposition to the assumption that china clay is dissociated into free alumina and free silica at 500–600°.

The hygroscopicity was determined by standing the materials for 24 hours at 25° over 10 per cent. sulphuric acid and noting the increase in weight; this was considered to be due to the water vapour absorbed. The following results were obtained by these investigators:

Temperature.	Percentage of water absorbed.		
	China Clay.	Alumina.	Silica.
110°	0.71	—	18.35
600°	0.33	9.80	15.93
700°	0.31	10.33	15.34
800°	0.37	10.75	12.85
900°	0.34	9.19	3.96
1000°	0.04	0.01	0.00

The low hygroscopicity of china clay compared with that of silica and alumina (600–900°) is extremely puzzling if it is assumed that the clay dissociates into free silica and alumina on heating. But in the light of the H.P. theory this is readily understood. If china clay were to dissociate as Mellor and Holdcroft assume, the product should have a much higher hygroscopicity than it possesses.

Another interesting investigation of Mellor and Holdcroft is their attempt to produce hydrous china clay from the dehydrated (heated) material. Samples of china clay which had been maintained for a long

time at 600–640° and still contained 1·04 per cent. of water (approximately 1 molecule of H_2O) were heated with water in an autoclave at 300° C. under a pressure of 200 atmospheres. The product, dried over P_2O_5 *in vacuo*, showed a loss on ignition of 3·63 per cent. (approximately 3·5 H_2O), the dehydrated china clay thus absorbing 2·5 per cent. or 2·5 molecules of water. This behaviour may be predicted from the Hexite-Pentite theory.

The Melting Points of Clays and other Aluminosilicates

[Technically, the melting point of certain aluminosilicates is of great importance. Especially is this the case with clays used for the manufacture of furnace linings and other refractory goods exposed to very high temperatures.]

The melting point of a substance has long been recognised as closely related to its chemical constitution, and C. Bischof[137] was the first to establish the existence of such a relationship. Unfortunately, his conclusions have been found to be incorrect in detail, but this does not prejudice his position of priority in this important subject.

[The fact should not be overlooked that the determination of the melting point of clays is so difficult that reliable conclusions based upon it are almost impossible of attainment in the present state of knowledge. What is usually termed the "melting point" is merely the point at which the influence of heat is sufficient to cause the bending of test pieces of an arbitrarily chosen shape (that of Seger Cones).

Clays do not appear to have any definite melting point, but, on heating, the amount of fused matter gradually increases, partly by the direct action of the heat and partly by the chemical action of the fused material on that which remains. Thus, a clay which is maintained for a sufficiently long time at a comparatively low temperature will show a similar amount of fusion or vitrification to another clay which has been raised to a higher temperature for a much shorter time. This fact is extensively used in the manufacture of stoneware, paving bricks and other articles of vitrified clay, as the loss of shape at a given temperature on prolonged heating is far less serious than when a higher temperature is employed for a much shorter time. In the manufacture of glazed goods, on the contrary, it is found that a little gloss, i.e. a more complete fusion, is obtained by means of a more rapidly rising temperature to which the goods are exposed for a comparatively short time. Hence, it is precisely because clays behave as if they were composed of a refractory skeleton, the pores of which are, on heating, gradually filled with a glassy material, that the manufacture of stoneware, porcelain, etc. becomes possible. If clays melted uniformly the result of heating them in kilns would not be the wares mentioned, but glasses and glazes.

It would remove much obscurity and many erroneous conclusions if the term "melting point" in the literature of clays and clay-working were replaced by the term *softening point*. The tests of the so-called melting point of clays and the temperatures associated with Seger Cones do not refer to the true melting point at all, but merely indicate the effect of the total forces acting on the material and resulting in a certain change in shape. This change is brought about by the production in the mass of a certain amount of fused or partially fused material and is the resultant of several forces, the individual influence of which it is extremely difficult to calculate.

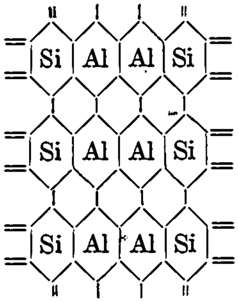
The generally accepted view of the phenomena observed in the melting point of clays is that they point to the fusion of the least refractory materials in the clay occurring first, this being followed by the gradual fusion of the remainder by the fused portion. This view is confirmed by the fact that clays do not appear to have a definite melting point like crystalline compounds, but a "range of fusion" such as is found on heating heterogeneous mixtures.

In view of the H.P. theory, it is not impossible that the low conductivity of clay for heat may lead to erroneous conclusions respecting the fusing points of articles made of clay by preventing the heat reacting on the interior of the mass. The results of prolonged heating at lower temperatures appear to confirm this view. To decide whether a clay has a sharp melting point (like a single chemical compound) or a

"melting range" (like a heterogeneous mixture) it would be necessary to keep it for a sufficiently long time at the lowest temperature at which any fusion appears to occur. The time required is so great that the cost of such tests becomes prohibitive, but until they have been made it is not logical to assume that the apparent behaviour of clays is necessarily opposed to their being definite chemical compounds and not mixtures. It is, moreover, not impossible that the progressive decomposition of the molecules containing substituted elements may make what are really true compounds behave as heterogeneous mixtures, though the former suggestion appears to afford a more probable explanation.]

That a close relationship does exist between the melting point and chemical constitution of a compound cannot be denied, and this being the case, the following statements are direct consequences of the H.P. theory:—

1. Clays are usually kaolinic acids which have undergone a partial polymerisation. In the theoretically possible compound:



$$18\,H_2O \cdot 18\,Al_2O_3 \cdot 36\,SiO_2,$$

one or more hydrogen atoms may be replaced by K, Na, Ca, Mg, Fe, etc.; one or more aluminium atoms may be replaced by Fe, Mn, Cr, Co, etc.; one or more silicon atoms may be replaced by Ti, Zr, etc. By such replacements compounds would be produced containing *very small percentages of certain elements* which would, nevertheless, have a marked influence on the melting point. It is obvious that this influence must be different with different elements. Not only must bases have a different effect on the melting point from that exerted by acids, but the various bases and acids will vary in their individual influence. Hence, the melting point of the material will be affected according as K, Na, Ba, or Ca, etc. replaces one or more hydrogen atoms, and whether a portion of the aluminium is replaced by Fe or Cr or Mn, etc., or whether Ti or Zr is substituted for part of the silicon.

Other variations in the melting point will occur according as a portion of the hydrogen, aluminium or silicon is replaced by analogous substances.

In all these cases the melting point is a periodic function of the atomic weight of the substituting element, i.e. there must be a definite relationship between the change in the melting point and the atomic

weight of the replacing element. As the atomic weight increases, the melting point of the clay may rise or fall.

2. Clays and aluminosilicates have varying $Al_2O_3 : SiO_2$ ratios. With any variation in the proportion of alumina or silica the melting point of the clay must also rise or fall.

3. The melting points of isomeric aluminosilicic acids and of the corresponding salts must differ from each other.

(See "Basis and Ring Isomerism," p. 63.)

The H.-P. Theory and the Facts

The available experimental evidence is not sufficient to prove completely the foregoing consequences of the H.P. theory regarding the relationship of the melting point and the chemical constitution of clays. Such facts as are known, however, are confirmatory of the theory.

Consequence 1 (p. 125)

It follows from the theory that the melting point of a clay must depend on the nature of the elements which replace some of the H, Si or Al in the theoretically pure kaolinic acid or clay. Opposed to this theory is the law of Bischof and Richter[726] which states that "equivalent amounts of fluxes have an equal influence on the melting point of any clay in which they occur."

[In order to obtain a numerical expression of this law, Bischof re-calculated the analyses of the clays he examined so as to show their molecular proportions, and arranged these as a formula of the type

$$O \cdot aAl_2O_3 \cdot bSiO_2,$$

in which the amount of base is constant, the two variables being the silica and alumina. Considering these variables alone, he suggested that the refractoriness of a clay might be represented by a coefficient or quotient (FQ). According to Bischof:

$$\text{Fire resistance Quotient (Bischof) } FQ_B = \frac{a^2}{b}.]$$

According to this law, it follows that equivalent amounts of potash, soda, ferric oxide, etc. should have an equal influence on the melting point of clays containing them. The following compositions of clays may be taken as an illustration :

$$
\begin{aligned}
0.5\,K_2O \cdot 9.5\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2,\\
0.5\,Na_2O \cdot 9.5\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2,\\
0.25\,K_2O \cdot 0.25\,Na_2O \cdot 9.5\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2,\\
10\,H_2O \cdot 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3 \cdot 12\,SiO_2,\\
10\,H_2O \cdot 5.5\,Al_2O_3 \cdot 0.5\,Mn_2O_3 \cdot 12\,SiO_2.
\end{aligned}
$$

These contain the same amount of fluxes, viz. 0·5 molecules, and should all have the same melting point. Actual determinations of the melting points of these clays show that this is not the case.

In direct opposition to Bischof and Richter's law are the extensive studies of Jochum[728] on a series of fireclays in connection with Seger Cones. The data obtained by Jochum are summarised in the following Table :

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Total Fluxes	Refractoriness in Seger Cones
1.	53.32	44.15	0.56	0.28	0.23	0.51	—	1.58	36
2.	52.24	43.43	0.87	—	0.32	0.35	—	1.54	35
3.	52.50	45.22	0.81	—	0.54	0.50	—	1.85	35
4.	52.74	45.81	1.00	0.15	0.05	0.54	—	1.74	36
5.	52.50	46.25	0.35	0.47	0.13	0.32	—	1.27	36
6.	52.33	45.81	1.30	—	—	1.43	—	2.73	35
7.	53.11	44.63	2.34	0.86	0.65	0.22	—	4.07	35-36
8.	52.74	46.00	1.07	—	0.23	0.24	—	1.54	35
9.	53.35	44.13	0.89	0.28	—	1.34	TiO_2 1.11	3.62	35
10.	53.35	43.35	0.83	0.24	—	1.43	—	2.50	35
11.	51.45	45.23	0.55	0.30	0.41	1.78	—	3.03	35
12.	51.57	45.70	1.31	0.86	—	0.77	—	2.94	35
13.	51.57	45.90	1.13	0.24	0.09	0.60	—	2.06	35
14.	51.90	46.10	1.14	0.24	0.09	0.60	—	2.07	35-36
15.	51.43	45.57	1.31	0.89	—	0.77	—	2.97	35
16.	55.00	40.60	2.86		1.30 Diff.		—	4.16	35
17.	57.00	37.00	3.66	0.57	—	1.77	—	6.00	35
18.	58.19	39.37	0.85	0.09	0.41	1.14	—	2.49	34
19.	52.34	40.11	2.54	0.25	0.91	3.87	—	7.57	33
20.	52.92	39.16	2.57	0.18	1.24	3.55	—	7.54	30
21.	52.48	39.16	2.55	0.18	1.23	3.52	—	7.48	32
22.	52.90	38.40	4.80	2.40	0.80	1.00	—	9.00	32

A glance at this Table will show the invalidity of Bischof and Richter's law. This is particularly noticeable with respect to clays Nos. 6, 7, and 8. The total percentage of fluxes in No. 6 clay is 2·73, in No. 7 clay 4·07 and in No. 8 clay 1·54, but the refractoriness of all three clays is the same (cone 35). Indeed, the clay with the lowest proportion of fluxes (No. 7) has, if anything, a higher degree of refractoriness than the other two. The figures in connection with clays No. 17 and 18 are even more striking. Clay No. 17 contains 6·00 of fluxes whilst No. 18 contains only 2·49, yet the refractoriness of No. 17 is a Seger cone higher than No. 18, i.e. cone 35 as compared with cone 34, whereas, according to the Bischof-Richter law, No. 17 should be considerably more fusible than No. 18. In the case of clays No. 19 and 21, the composition is practically identical, but the refractoriness is different.

[Seger[730] has pointed out that the Bischof-Richter law is only applicable to clays containing a very small proportion of basic oxides, i.e. to the most highly refractory clays, and that it is quite useless for second-grade fireclays and clays used for building purposes.

Richter[730] found that the form in which the silica is present in a clay, i.e. whether combined or in the free state, has a profound influence on the melting point. Hence, as Seger has pointed out, the resistance of clay to heat does not depend on the composition of the material as a whole, but on the compounds present in it and on their state of aggregation. This fact has been repeatedly confirmed and is well known to all

manufacturers of refractory goods. Indeed, the remarkable variations in fireclay deposits are a daily source of anxiety to those using them. For this reason, and because he regarded the variety of minerals present in most clays as rendering abortive all consideration of the melting point of any clay as a whole, Seger[730] insisted that it is first necessary to free the clay as far as possible from sand, silt, and other impurities by washing, and then to study the melting point of the purer product thus obtained. He therefore applied Bischof's Quotient to that portion of the clay which is sufficiently fine to be washed out by a current of water flowing at the rate of 0.18 mm. per second (i.e. on the nearest approach to " pure clay " obtainable on mechanical elutriation of a commercial clay and termed by him " clay substance," but more accurately *clayite* in the case of china clay by J. W. Mellor[708], and *pelinite* in the case of plastic clays by A. B. Searle[732]). With this purified material Seger obtained results which agreed much better with the actual fusion tests. As, however, serious discrepancies still existed—even among the higher-grade clays—Seger eventually suggested the following formula applied to the clayite or pelinite above mentioned, and not to the material as a whole :

$$\text{Fire-resistance Quotient (Seger) } FQ_s = (a+b)\frac{a}{b}.$$

This formula, though applicable to a larger number of clays than Bischof's, is, like the latter, extremely limited in its application and is far from reliable, and Seger

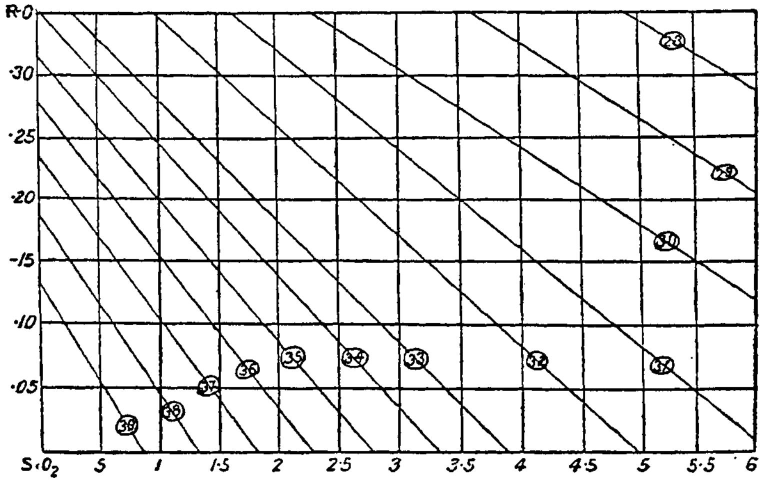


FIG. 1.—Ludwig's Chart

himself found several fireclays and kaolins in regard to which it proved impossible to obtain an agreement between his formula and the results of actual fusion tests. That Seger recognised this is clearly shown in the following statements in his " Collected Papers " : " Both Bischof's and my coefficients only give approximate figures, as the fusion of clays involves several important physical factors which must inevitably be omitted from any method of calculation." " It is unwise to attach much importance to any coefficient, because it cannot include the variations in the size of the grains of clay this factor being quite as important as the composition of the material. Thus, silica in an extremely finely divided state acts energetically as a flux, but coarser silica increases the heat resistance of some clays to which it is added ! " Seger also laid great stress on the irregularity of composition observed in clays, and declared them to be " not homogeneous, but merely mixtures of various minerals of which the largest proportion is 'clay substance.' " " Hence, any figure which it is claimed represents the melting point based on the composition of the material can only be rough approximations."

When Seger's quotient is applied to the analyses shown in the Table on page 127, the results obtained are so conflicting that it is impossible to trace any direct con-

nection between Seger's quotient and the Seger cone numbers in the last column of the Table. It is, however, only fair to observe that the temperatures indicated by these Seger cones are not the true melting points of the clays, but only the "softening points," and Bischof has shown there is no simple law connecting the temperature at which Seger cones bend with that at which they melt.

A method of calculation similar to those of Bischof and Seger, but differing in the manner of its representation, is that of T. Ludwig[706], who assumed that the fluxes in a clay are in the form of a solid solution with the clay as a solvent, and arranged the composition of a clay as a formula with alumina as unity thus:

$$x\,RO \quad Al_2O_3 \quad y\,SiO_2,$$

plotting x as ordinates and y as abscissæ. Ludwig obtained a chart (Fig. 1) in which the diagonal lines represent the limits of the Seger cones marked thereon, so that the "melting point" of a clay is represented in terms of these cones. This chart is in close agreement with the experimental observations of many fireclays and kaolins, but is entirely unreliable for clays in which the total fluxing oxides exceed 6 per cent. Ludwig attributed its failure to the heterogeneous nature of clays and to the irregular distribution of the fluxes in them.

The relationship between the composition of clays and their melting point has also been investigated by H. Seger'[30], who studied the melting point of mixtures of silica and alumina and of silica and kaolin to which sufficient felspar was added to keep the alkali-content of the various mixtures constant.

Seger found that mixtures of free silica and alumina behave in a manner similar to mixtures of kaolin and pure quartz-sand, so far as the melting points are concerned. In both cases the larger the proportion of silica the lower the melting point, until a material is obtained with a molecular ratio of 1 Al_2O_3 : 17 SiO_2, after which the addition of more silica increases the melting point until practically pure silica is obtained. These results are summarised in the curve shown in Fig. 2 (see also p. 132).

That some definite relationship does exist between the composition and the softening point of clays is shown by the existence of a regular series of Seger cones. These are composed of mixtures of pure kaolin with marble, felspar, and quartz in atomic proportions, the whole being reduced to an exceedingly fine powder. Notwithstanding the fact that the purest possible materials are used in the manufacture of these cones, no definite general formula has been found for connecting the fusing point of these cones with their composition. Seger laid special emphasis on the undesirability of attempting to correlate the Seger cones with definite temperatures. "I permit the preparation of a scale of comparison between my cones and definite temperatures," he wrote, "with the greatest unwillingness, more especially as I have found no means of comparison for the highest cones." Seger's caution and modesty are well known, so that it is interesting to note that later investigations have proved that, with trifling exceptions, all the cones above No. 10 correspond very closely to definite temperatures, provided that the rate and other conditions of heating are favourable and constant, but that slight variations in the condition of heating cause serious discrepancies in the behaviour of the cones. It should, however, be noted that Seger's cones do not show the melting points of the mixtures composing them, but only the resultant of the various forces which cause them to bend to a definite extent. Whether there is any relationship capable of simpler expression numerically between the bending temperatures of Seger cones and their true melting points remains to be proved. Meanwhile, in view of the misuse of terms in the literature of the subject, too much emphasis cannot be laid on the fact that Seger cones merely indicate the *softening points* of the materials of which they are made. These softening points, together with the molecular composition of the cones, are shown in the Table on the next page.

SEGER CONES AND TEMPERATURES

Estimated Temperature ° C.	Cone No.	Molecular Composition			
		K_2O	CaO	Al_2O_3	SiO_2
1320	11	.25	.58	1	10
1350	12	.21	.50	1	10
1380	13	.19	.53	1	10
1410	14	.17	.39	1	10
1435	15	.14	.33	1	10
1460	16	.13	.29	1	10
1480	17	.11	.26	1	10
1500	18	.10	.23	1	10
1520	19	.09	.20	1	10
1530	20	.08	.18	1	10
*	21	.07	.15	1	10
*	22	.06	.14	1	10
*	23	.06	.13	1	10
*	24	.05	.12	1	10
*	25	.04	.11	1	10
1580	26	.04	.10	1	10
1610	27	.02	.03	1	10
1630	28	—	—	1	10
*	28½	—	—	1	9
1650	29	—	—	1	8
*	29½	—	—	1	7
1670	30	—	—	1	6
1690	31	—	—	1	5
1710	32†	—	—	1	4
1730	33	—	—	1	3
1750	34	—	—	1	2.5
1770	35	—	—	1	2
1920	40	—	—	1	—

* These cones are not manufactured, as their Estimated Temperatures lie too close to neighbouring cones, and are somewhat irregular.

† Pure silica behaves like cone 32.

It will be observed that there is a fairly regular difference in temperature between consecutive cones, but this is not sufficiently constant for any simple law to be found from a graph of the cone numbers and temperatures.

Simonis[70a] has studied mixtures of kaolin, quartz, and felspar in connection with Seger cones and found that the felspar acts as a constant and neutral flux. He also concluded that the softening point of such a mixture might be represented numerically by a "refractory index," using the symbols k for the percentage of kaolin, s for that of quartz, and f for that of felspar. According to Simonis, if k is greater than $\frac{s}{3}$ the "refractory index" will be $R = \frac{s}{3} - f + 60$. For bodies high in silica, in which $\frac{s}{3}$ is greater than k, the "refractory index" is $\frac{2s}{3} - k - f + 60$. The value of this "refractory index" in terms of Seger cones is given in the accompanying Table :—

Refractory index ..	17.5	22.6	28	33.7	39.2	44.6	50	57.6
Seger cone	14	15	16	17	18	19	20	26
Refractory index ..	65	72	80	89	102	114	127	141
Seger cone	27	28	29	30	31	32	33	34

It will be observed that there is no simple relationship between Simonis' Refractive Index and the corresponding Seger Cones.

In short, the Bischof-Richter law, together with the various modifications of it and the other attempts to correlate the melting points of clays with their chemical constitution here noticed, which are not in accordance with the H. P. theory, is shown by the above evidence to be erroneous. Further investigations must show that, in accordance with the H.P. theory, the true melting point of a clay (not the "softening point") is a periodic function of the atomic weight of the replacing elements.

[That this relationship has not been found is, in part, due to the difficulties experienced in melting the purer and therefore the most refractory clays, and also to the very widespread belief that clays are heterogeneous mixtures and not true chemical compounds. The general evidence in favour of the H.P. theory is, however, so strong as to make this consequence of it highly probable, even though the experimental evidence at present available in respect of melting points is of little or no assistance. In due time the various germs of truth in Bischof's and other theories will emerge from the obscurity in which they have so long lain, in consequence of the non-existence of a correct theory as to the constitution of clays and allied substances.]

It is highly probable that the melting point will be lowered by the substitution of elements of higher atomic weights. Such an effect has been observed by G. Jantsch[729] in other complexes with the general formula :

$$3\,Mo \cdot X_2O_3 \cdot 6\,N_2O_5 \cdot 24\,H_2O,$$

where $Mo = MgO \cdot MnO \cdot NiO \cdot CeO \cdot ZnO$, and
$X_2O_3 = La_2O_3 \cdot Ce_2O_3 \cdot Pr_2O_3 \cdot Nd_2O_3 \cdot Sm_2O_3 \cdot Gd_2O_3$.

This is shown in the following Table :

	Mg	Mn	Ni	Ce	Zn
La	113.5°	87.2°	110.5°	101.8°	98.0°
Ce	111.5°	83.7°	108.5°	98.5°	92.8°
Pr	111.2°	81.0°	108.0°	97.0°	91.5°
Nd	109.0°	77.0°	105.6°	95.5°	88.5°
Sm	96.2°	70.2°	92.2°	83.2°	76.5°
Gd	77.5°	——	72.5°	63.2°	56.5°

The divalent manganese appears to behave in an exceptional manner which cannot, at present, be explained.

Consequence 2 (see p. 126)

The melting point of silicates containing no alumina increases with the silica-content. Thus, bisilicates fuse at a higher temperature than monosilicates, and trisilicates are more difficult to fuse than bisilicates.

In most cases, the physical properties of complex substances differ from those of their constituents. This is also the case with aluminosilicates in which, according to the researches of C. Bischof, a lower fusing point accompanies a higher silica-content, the aluminosilicates which are rich in silica being more fusible than those relatively poor in silica.

A glance at Fig. 2, which shows the results obtained by Seger[730] on mixtures of pure silica and alumina (see p. 129) shows :—

1. An increase in the proportion of silica is accompanied by an increased fusibility.

2. The melting point, or more strictly the softening point, diminishes with an increase in the proportion of silica until the mixture with a ratio $Al_2O_3 : SiO_2 = 1 : 15$ is reached, after which there is a change in the direction of the curve until a ratio 1 : 17 is reached, after which an increase in the proportion of silica is accompanied by an increase in the melting point.

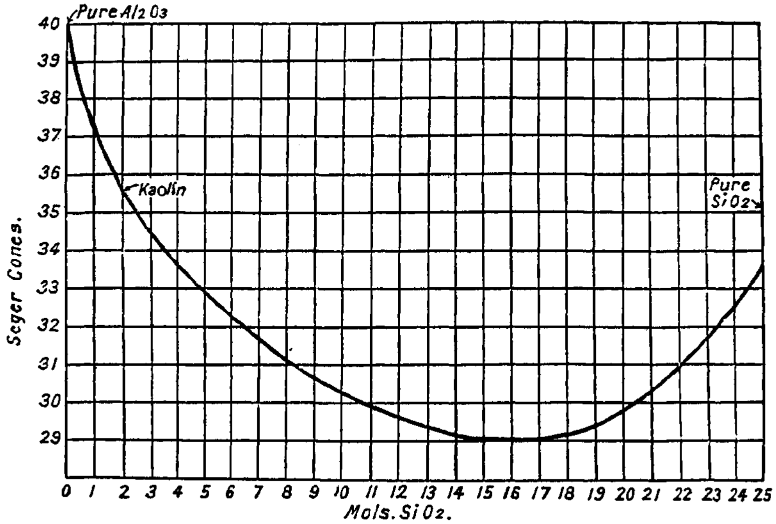
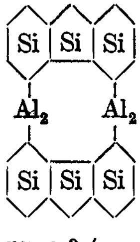


FIG. 2.—Relation of Softening Point to Composition (Seger)

The flattening in the curve indicates the formation of a compound, and as glasses are known with a ratio of $Al_2O_3 : SiO_2 = 2 : 36$, the curve appears to indicate the existence of a secondary type of such a glass. The compound Al_2O_3, 17 SiO_2 would then have a high molecular weight and the following structural formula :—



Consequence 3 (see p. 126)

No experimental evidence is available for proving the correctness or otherwise of this consequence of the H.P. theory, but further investiga-

tions of clays and aluminosilicates will, in all probability, lead to the definite confirmation of this theory.

. . . .

In connection with the foregoing observations the behaviour of the so-called *mineralisers*[733] may be mentioned. The ones most generally used are the chlorides of calcium, magnesium, manganese, aluminium, and silicon, the fluorides of calcium, sodium, potassium, magnesium and silicon, the tungstates of potassium and lithium, the borates of magnesium, calcium and sodium, the phosphates of potassium, magnesium, etc. These mineralisers appear, in many cases, to form sodalitic compounds with silicates (see *Sodalites* p. 59) and, on adding a mineraliser to a compound or mixture, the melting point of the substance is considerably reduced.

Mineralisers play an important part in the synthesis of various minerals and without them some minerals cannot be produced.

The Cause of Plasticity in Clay

Before concluding this chapter, a few words may be added on the plasticity of clay.

The authors agree with Seger[221] in terming those substances plastic which possess the power of absorbing and retaining fluids in their pores in such a manner that the mass may be given any desired shape by kneading or pressure, this shape being retained after the pressure has been removed. It is a further condition that if the fluid is removed, the substance shall retain its shape unchanged.

A number of theories[221a] have been formulated to explain the causes of the plasticity of clays.* The authors of the present volume consider those theories are the most probable which assign the chief cause of plasticity to the "water of constitution" in clays.

From this it follows that :

A. The more OH-groups a clay contains in the form of "water of constitution," the more plastic must it be.

B. By separation of the OH-groups on an increase in temperature of the clay, or by the replacement of hydrogen by a base, the plasticity must be reduced or completely destroyed.

These consequences of the theory are fully confirmed by facts.

Thus, Seger[221] found that if a cream or slip made of clay and water is allowed to settle and the clear water decanted, the pasty sediment will be so stiff that it can bear the weight of a glass rod without the latter sinking into it. If, however, to the water used for making the slip a few drops of caustic soda, sodium carbonate solution or water-glass are added, so that the water is rendered feebly alkaline, a remarkable change occurs. The slip becomes considerably thinner and more fluid,

* The chief of these are summarised in "British Clays, Shales, and Sands."[704]

part of the material settles immediately to the bottom as a solid substance and the supernatant liquid requires a very long time before it becomes clear. If, now, a few drops of acid are added to the mass, it becomes so stiff that the vessel in which it is contained may be inverted without spilling the contents. On drying to a definite volume, the acidulated mass will be found to be much more plastic than the original clay and the alkaline mass will have lost almost all its plasticity. It is highly probable that in Seger's experiment, the prolonged action of water or acids on the clay had effected a partial separation of the alkalies it contained, whereby an increase in plasticity resulted, due to the cause indicated in Conclusion A above[221a].

By the action of alkali, a partial substitution of H by the alkali may also occur and, as indicated in Conclusion B, this is the reason the plasticity is reduced.

E. v. Sommaruga[222] has shown, by analysis, that aluminosilicates of the alkalies and alkaline earths lose part of their base on washing.

In agreement with Conclusion B, there is the further fact that clays lose their plasticity at high temperatures, at which the water of constitution is also driven off.

The fact that some hydrous-aluminosilicates, such as the zeolites, are non-plastic is not in opposition to the above theory as to the cause of plasticity, as the introduction of a definite proportion of base so as to form a salt—and zeolites are true salts—completely destroys the plasticity.

[The term plasticity, as ordinarily used, includes so many other properties that the interpretation of experimental results is extremely difficult. Moreover, no generally accepted method of measuring plasticity has yet been devised, all those now in use being open to several objections, the chief of which is that they measure some property closely allied to plasticity—such as tensile strength, adhesion, viscosity, binding power, etc., but not the plasticity itself.

Again, Drs. W. and D. Asch make no mention of the close connection between the colloidal material present and the plasticity of clays, nor do they explain how it is that quartz, calcium fluoride and a number of other substances of widely different constitution and composition have been found by Flett, Atterberg and others to be plastic when in a sufficiently finely divided state.

If it is really a fact that extremely finely divided silica which is free from constitutional water can become truly plastic, the hexite-pentite theory will require modification. In the present state of knowledge it is, however, extremely difficult to decide whether the substances just mentioned do become truly plastic or whether they merely become more cohesive.

Several investigations, including those by Rieke[707], have shown that the loss of plasticity when a clay is heated is not proportional to the loss of "water of constitution." A certain amount of plasticity remains, even when all the water has been removed from the clay, provided that the removal has been effected at a low temperature. For this reason Rieke and others have concluded that the loss of plasticity on heating is due to the physical rather than to the chemical nature of the clay. An equally correct conclusion and one which is, moreover, in conformity with the hexite-pentite theory, is that the loss of "water of constitution" is accompanied by polymerisation phenomena which materially reduces the plasticity and necessarily involves a lack of proportionality between the loss of water and of plasticity when the clay is heated, especially as, under such conditions, the plasticity is lost at a greater rate than the "water of constitution."

The reader interested in this subject will find further details in the translator's "British Clays, Shales, and Sands," in which the conclusion is reached that the plasticity is partly due to the extreme smallness of the clay particles, partly to the shape, texture and physical nature of these particles, and only slightly to their chemical composition.

Considering the great stability of the clay molecule, it certainly appears to be quite as likely that the action of a few drops of acid or alkali on a considerable weight of clay may be due to the colloidal material in clay as to any change in the chemical composition of the clay molecule of the nature suggested above. Moreover, it is difficult to understand why china clays and kaolins should be so slightly plastic compared to ball clays yielding such remarkably similar results on analysis, unless plasticity originates largely in the physical, rather than in the chemical nature of clay. This may, of course, be due to somewhat different chemical structure (isomerism or polymerism) and the hexite-pentite theory is *a priori* in favour of such an explanation as accounting for the physical differences.

The whole subject of plasticity is, however, so complex, that no definite theory as to its cause has yet been found which will satisfy the whole of the facts. Under these circumstances, the theory suggested by Drs. W. and D. Asch takes its place amongst the numerous other serious attempts to ascertain the cause of this very elusive property of clays. In the opinion of the translator, however, the present application of the hexite-pentite theory to plasticity is attempting too much. The hexite-pentite theory is so valuable in its relation to the chemical composition of clays that it would be a pity to prejudice its acceptance by prematurely extending its application. When more is known of the nature of plasticity, it is not improbable that the value of this theory, in regard to plasticity, may be much greater than now appears to be the case.

The Colour of Bricks and other Articles of Burned Clay

The red colour of building bricks is usually attributed to the presence of free ferric oxide in the burned clay; that of Staffordshire "blue" bricks and clinkers is generally considered to be due to the production of a ferrous silicate by the reducing action of the kiln gases on the ferric oxide in the burned clay.

It is, however, a curious fact that the best red bricks cannot be made by adding ferric oxide to a clay, though the use of this substance does produce a low grade of red brick with a very irregular colour. Moreover, ordinary "red oxide of iron" dissolves readily in hydrochloric acid, but the colour of a finely-ground red brick is not removed by cold acid, nor can such a powder be completely bleached even by boiling with hydrochloric acid for several hours. Again, the clay used for blue Staffordshire bricks produces goods of a bright red colour if burned in an oxidising atmosphere, the blue colour being only formed when reducing gases are present. If the temperature of the kiln has not been excessive, and the atmosphere is made strongly oxidising, the blue colour is replaced by a bright red one, this transformation of blue and red and *vice versâ* being capable of being repeated indefinitely as long as the temperature is carefully regulated.

The generally accepted opinion that a simple ferrous silicate is the cause of the "blue" colour is not borne out by synthetic ferrous silicates, the colours of the latter being quite different.

These facts all point to the colour of bricks being due to an aluminosilicic anhydride containing iron in such a form that it can be readily converted from the ferric to the ferrous state and *vice versâ*. The structure of silicates in which the colour is due to a chromophore group containing a metallic oxide is described in greater detail in a later section on "Coloured Glasses," in which the state of combination of the metal is explained by the aid of the H.P. theory.

Seger[730] and others have exhaustively investigated the relationship between the iron contents of numerous clays and the colours of the bricks obtained therefrom, but have not been able to find any definite correlation between the two. In many instances clays which contain 5 per cent. or more of iron calculated as ferric oxide, burn to a pale buff or primrose tint, whilst other clays with only 3 per cent. of iron oxide produce bricks of a strong dark red colour. The lower-grade fireclays and other buff-burning clays do not contain less iron than red-burning clays, but they must contain it in a different form. There is evidence in support of the view that in buff-burning clays the iron is chiefly in the form of pyrites, whilst in red-burning clays it is in the form of a ferrosilicic or ferro-alumino-silicic acid, analogous to clay in which one or more of the hydrogen atoms have been replaced by an atom of iron. Seger also found that clays rich in alumina as well as iron, usually burn to a buff rather than to a red tint.

It is interesting to note, in this connection, that if a red-burning clay is washed with dilute hydrochloric acid a large part of the colouring matter will be removed, and if the clay is then dried and burned it will be of a yellowish red colour. No treat-

ment with acid has yet been found, however, which will remove all the iron without destroying the clay.

If buff-burning clays are brought into momentary contact with flame in the kiln a reddish tint will form on their surface, as though a portion of the combined iron were set free as ferric oxide. No satisfactory explanation of this phenomena has yet been published, as the amount of red substance formed is too small for analysis; the production of such "flame-flashed" goods is, however, well known to all makers of fire-bricks.

If chalk is mixed with a red-burning clay, the bricks produced at temperatures below about 800° C. are red, but above this temperature the chalk reacts with the iron compound and the bricks are quite white and might be supposed to be quite free from iron. The nature of this white compound of lime, iron and clay has never been ascertained, but in the light of the H.P. theory it would appear as if the lime had destroyed the chromophore group—forming a new ferruginous silicate—and so had deprived the iron of its colouring power.

The whole subject of the colour of burned clays is of great technical importance, but hitherto it has been subject to so many assumptions which have passed as explanations that very little scientific investigation has been made. Clayworkers have been content to accept the assumption that the red colour of certain bricks is due to the free ferric oxide in the clay without troubling to ascertain how it is that 5 per cent. of iron oxide is without effect on the colour of the raw clay and yet produces such an intense colour when the clay is burned. That some change must occur in the combination of the iron is obvious and the view published some years ago by the translator of the present work, that a large proportion of the iron occurs in the form of ferrosilicic acid (? nontronite, $H_4 Fe_2 Si_2O_9$) which, on heating, is decomposed into water, silica and free ferric oxide, certainly agrees with a number of the important properties of red-burning clays. Whether the iron is in the form of a ferrosilicic acid or of a substituted group in an aluminosilicic acid it is, at present, almost impossible to determine experimentally.]

XII

The Ultramarines

Historical Review

Since 1828, many fruitless attempts have been made to ascertain the true cause of the colour of the ultramarines. Those investigators who consider ultramarine to be simply a "mixture" or a "solid solution" have, naturally, endeavoured to find a "colouring principle," the nature of which varies according to the various authors. Thus, according to Gmelin[245] and Breunlin[246], the "colouring principle" of ultramarine is sulphur; Elsner[247], Kressler[248], Guyton Morveau[249], Prükner[250], and Varrentrapp[251] consider it to be iron sulphide, but Brunner[252] has contradicted this by producing a blue from materials quite free from iron, which colour is in every respect equal to that produced from ferruginous clays. According to Unger[253], the blue colour of ultramarine is due to nitrogen compounds, but Büchner[254] has disproved this by showing that "ultramarine" contains no nitrogen. Stein[255] has suggested that ammonium sulphide, mixed with the ground mass in a state of "molecular fineness," is the colouring matter of "ultramarine," and Rohland[256] has stated that "ultramarine" contains a "colour-carrying substance," or *chromophore,* whose composition he has not published.

On the contrary, those investigators who consider the ultramarines to be definite chemical compounds seek for the source of the colour in

the arrangement of the smallest particles of this compound, i.e. they regard the colour of ultramarine either as a constitutional property or seek its origin in definite atomic complexes which form definite chemical compounds with the essential constituent (silicate) of the ultramarines. Among others in the first class is included Ritter[257], who considers that "there can be no question of a colouring principle, as the *whole* of the ultramarine forms a chemical compound because, as previously shown, one form of such substances may be colourless, yet may, under certain conditions, be converted into a coloured compound without the introduction of any new substance—a comparatively clear indication that here, as everywhere, the colour is due to the arrangement of the "smallest particles."

R. Hoffmann[258] is one of those who consider that the cause of the colour is to be found in definite radicles contained in the ultramarine. He has referred frankly and clearly to sulphonates which can add or lose sodium, oxygen, and sulphur, forming various colours.[259] "These changes occur in a similar manner to those in the side chains of organic compounds; addition, substitution, and subtraction changes may occur without destroying the combination with the silicate molecule."

It is clear that Hoffmann's conception of the constitution of ultramarine is the one which most closely resembles that of the authors of the present volume.

In this connection, the following extracts from Hoffmann's interesting work on ultramarine are of value:[260] "for the present it is sufficient to state that the formation of green and blue ultramarines and their behaviour towards various reagents confirm the view that the sodium added in the form of oxide must be more firmly united to the elements of the kaolin than is the sulphide, and that it alone takes part in the further conversion of white into blue and green ultramarine. Consequently, it is possible to distinguish a silicate side from a sulphide side in the ultramarine molecule without in any way disturbing the combination of the elements as a whole."

Hoffmann[261] was also the first to claim the chemical individuality of ultramarine and to confirm this by means of microscopical investigation.[262] He was also the first to show that it is not correct to speak of one ultramarine, but rather of ultramarine compounds; he endeavoured to classify these into those "rich in silica" and those "poor in silica."

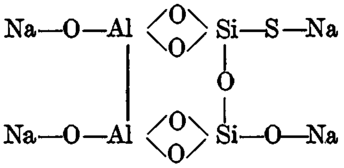
The view that there are several ultramarines and that some, at least, of these are chemical compounds, has been independently adopted by Phillipp[263], Szilasi[264], Heumann[265], Guckelberger[266], etc. At the same time, it should be noted that Hoffmann has doubted the chemical individuality of several ultramarines, including "ultramarine green."

"Ultramarine green" is generally understood not to have the properties of a chemical compound.[267] It is considered to be either a mixture of ultramarine blue and a yellow substance or as ultramarine blue to which sodium sulphide, etc. has adhered.

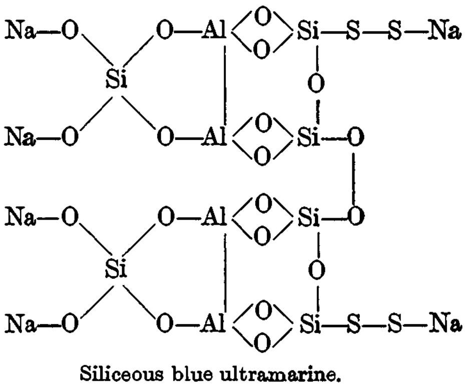
For this reason Guckelberger[268] examined "ultramarine green" microscopically and found it to be a perfectly uniform, transparent, sea-green substance. No traces of blue particles or of those intermediate between green and blue were discernible. Hence, Guckelberger concluded that "ultramarine green" is a single chemical compound.

It is surprising to find that, as early as 1878, R. Hoffmann[269] expressed an opinion on the nature of the bond of the sulphur-group in the ultramarines which is very similar to that of the authors of the present volume. He also expressed the belief that part of the oxygen in the silicate molecule is replaceable by sulphur. "The existence of a sodium silico-aluminate in which that part of the oxygen which is in closer combination with sodium can be replaced by sulphur—such silico-sulphonates behaving like free sodium monosulphonate (from which higher sulphonates may be produced by combination with sulphur and loss of sodium, without the silicosulphonate being decomposed)—would be sufficient to explain the formation of ultramarine by the ordinary method of preparation and also its chemical behaviour towards other substances."

R. Hoffmann[734] endeavoured to find satisfactory structural formulæ for white ultramarine, siliceous blue ultramarine, etc., and for this purpose made use of the silicate formulæ proposed by K. Haushofer[735] to obtain the following :



White ultramarine.



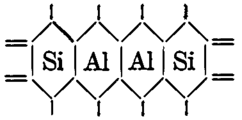
Siliceous blue ultramarine.

Hoffmann admitted, however, that these formulæ were more fantastic than probable.

A New Ultramarine Theory

The formulation of the authors' new hexite-pentite theory of the constitution of the silicates, and the existence of an extensive literature of ultramarine, naturally suggest the application of the theory to the ultramarine compounds. The absence of a general theory of the composition of the silicates appears to be the chief reason why the key to the chemical constitution of the ultramarines has not yet been obtained, in spite of the innumerable experiments which have been made.

For example, the following hydro-aluminosilicate :



$$\mathring{H}_{12}\mathring{H}_4(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

contains two kinds of OH-groups :

1. Aluminium hexite hydroxyl (or *a*-hydroxyl).
2. Silicon hexite hydroxyl (or *s*-hydroxyl).

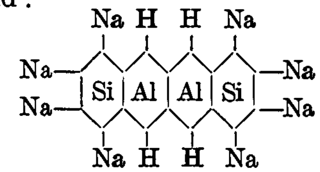
The four *a*-hydroxyls must obviously behave differently from the twelve *s*-hydroxyls. As a matter of fact, the hydrogen in the *a*-hydroxyls is readily replaced by monovalent acid radicles such as—NO_2 —$CrO_2 \cdot OH$, —SO_2OH, etc. The hydrogen of the *s*-hydroxyls is, on the contrary, more easily replaced by basic groups.

In the hexite-pentite theory of ultramarines, the *a*-hydroxyls play a special part. The substitution of acid radicles for hydrogen in the *a*-hydroxyls is specially noticeable as a characteristic property of the compound $\mathring{Na}_8\mathring{H}_4(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$ first observed by Silber for which no explanation has, hitherto, been obtainable.

On heating a mixture of kaolin with an excess of soda, to redness, and washing the calcined product with water, Silber obtained the compound :

$$(Si_2Al_2Na_2O_8)_6 = \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}).$$

If this substance is treated with dry hydrochloric acid gas at 150°, one-third of the sodium separates out as sodium chloride and there remains the compound :

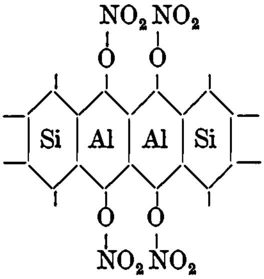


This compound, contrary to the original substance, possesses the remarkable property of not replacing its sodium by silver when treated with a solution of silver nitrate. Instead of replacing the sodium, the silver is precipitated as oxide.

Silber[223] gives this substance the formula $Si_6Al_6Na_4O_{23}$, but he has

undoubtedly overlooked the presence of hydrogen in it. The separation of Na by the action of HCl can only occur when the Na is replaced by H, for a temperature of 150° is much too low for OH-groups to separate in the form of water.

On the assumption that in the α-hydroxyls the hydrogen can be replaced by acid radicles, the behaviour of the compound $\overset{\circ}{Na}_8\overset{\circ}{H}_4(\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si})$ with $AgNO_3$ may readily be explained. By loss of Ag_2O and H_2O the compound :



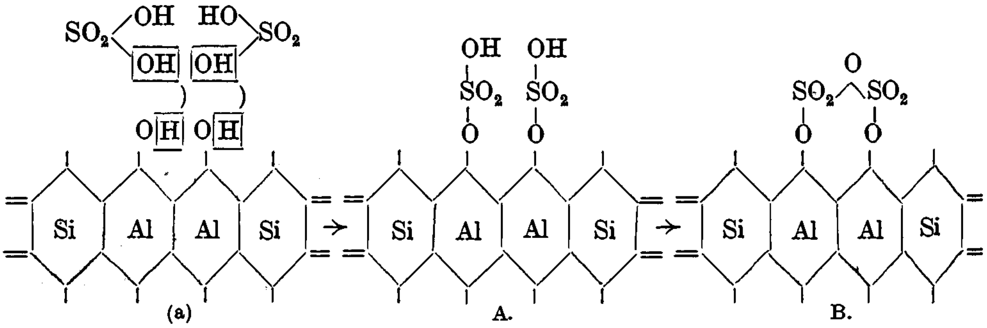
is formed.

If this view is correct, a maximum of four atoms of silver can be separated for each twelve atoms of silicon. The correctness of this consequence of the theory must be proved experimentally.

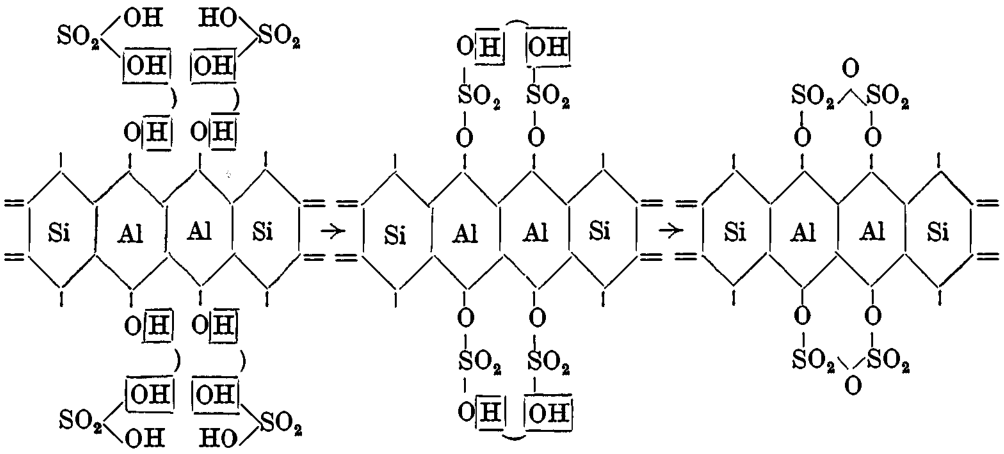
The above theory permits the prediction that the hydrogen in the α-hydroxyls may be substituted by the most varied monovalent inorganic or organic acid radicles, and that in all compounds of the $\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si}$ type, only four of these acid radicles can be taken up.

The aluminosilicates in which the hydrogen of the α-hydroxyls can be substituted by monovalent acids or acid radicles may conveniently be represented by the terms *A*-aluminosilicates or Σ-aluminosilicates.

The mode of formation of the *A*-aluminosilicates may be made clear by means of a few examples. The production of these compounds may be explained as due to splitting off the elements of water. Thus, from 2 or 4 mols. $SO_2{<}^{OH}_{OH}$ and the hydrate $\overset{\circ}{H}_{12}\cdot\overset{\circ}{H}_4(\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si})$, the following *A*-aluminosilicates will be produced :



(a) A. B.

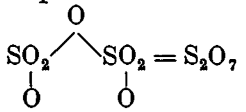


(b) C. D.

The compounds A, B, C, D are acids or acid anhydrides.

The hydrogen atoms of the sulpho-groups in A and C and the *s*-hydroxyl groups may be partially or completely replaced by a base, whereby acid or normal salts will be produced.

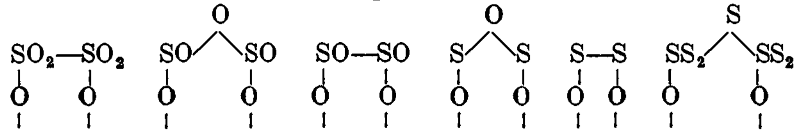
In ultramarines, the group



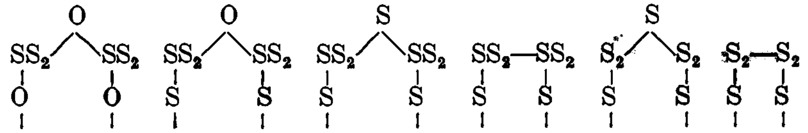
(a)

plays a special rôle. This atomic complex has the power, under certain conditions, to split off oxygen atoms and to take them up again, or to replace them partially or completely by sulphur atoms. Thus, there may be formed from S_2O_7 the following :

Sulphonates



S_2O_6 (b) S_2O_5 (c) S_2O_4 (d) S_2O_3 (e) S_2O_2 (f) S_7O_2 (g)



S_6O_3 (h) S_8O (i) S_9 (k) S_8 (l) S_7 (m) S_6 (n)

etc. etc.

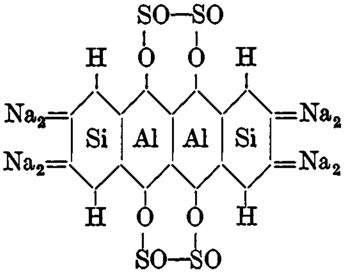
The sulphonates are very labile radicles and can be converted into one another, under certain conditions, by the loss or addition of oxygen or sulphur atoms or by the substitution of atoms of oxygen for those of sulphur and *vice versâ*. The atomic complexes *a, b, c, d, e,* etc. are anhydrosulphonates, but they may also enter the above *A*-aluminosilicates A and C as hydro-compounds.

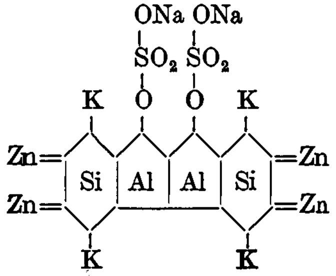
The Sulphonates as Chromophores

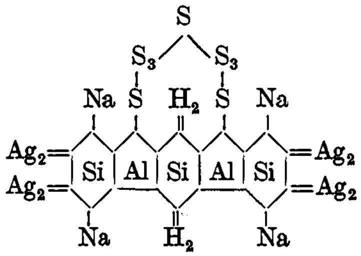
The study of the *A*- and Σ-aluminosilicates containing sulphonate groups has shown that these substances may be regarded as chromophores in the sense in which this term is used in Witt's theory.*

The introduction of a sulphonate group in this way into a hydro-aluminosilicate is not sufficient to form a coloured body. There must also be one part of the hydrogen of the *s*-hydroxyls or the total hydrogen of the *A*- or Σ-hydro-aluminosilicates replaced by mono- or divalent basic atoms. Such colour-stuffs may be termed "ultramarines."

Ultramarines are, therefore, in terms of the hexite theory, such compounds as :







etc. etc.

Following the suggestion of M. Schütz[224] it is convenient to regard the change from yellow to orange, red, bluish violet, violet, blue, blue-green and green as a deepening of the colour ; the reverse change from blue-green to blue, etc. as a lightening of the colour.

R. Nietzki[225] has formulated a law representing the relation

* Witt's theory is described in further detail in a later chapter on the chemical constitution of coloured glasses, p. 246.

between the change of shade in a pigment and its composition. According to this, the pigments of the simplest constitution are yellow ; with increasing molecular weight the yellow colour changes into red, violet and blue. Later researches by Krüss and S. Oeconomides[226], H. W. Vogel[227], and E. Koch[228] have shown that Nietzki's law is of general application, but that there are certain exceptions to it in which an increase in the molecular weight accompanies a lightening instead of a darkening of the colour.

With increasing molecular weight, the sulphonate group can produce either a deepening or a lightening of the colour.

As it is not sufficient merely to have a sulphonate chromophore in order to form a hydro-aluminosilicate pigment, and the introduction of a base into an acid is necessary, it is clear that the nature of the base must exercise an important influence on the shade. An increased molecular weight may thus cause either a lightening or darkening of the colour. In all probability, the molecular weight of the original substance of the pigment (i.e. the aluminosilicate itself) is also of importance in connection with the shade of colour produced.

Enough has been said to enable the various facts relating to ultramarines to be explained in a simple manner. Apart from this, however, the theory shows the manner in which further investigations—both practical and academic—may most usefully be carried out in connection with these highly important pigments.

The Hexite Theory of Ultramarines and the Facts

From the ultramarine theory developed above, a series of Consequences result. It is important to see how these agree with the facts.

A

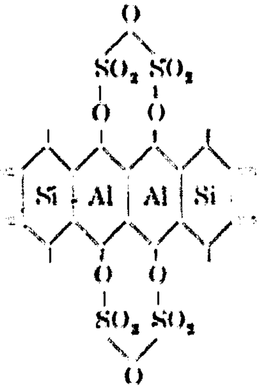
Theoretically, the composition of the ultramarines may be predicted. It is, in fact, highly interesting to calculate the formulæ of a large number of analyses in order to see how far they confirm the Consequences of this theory.

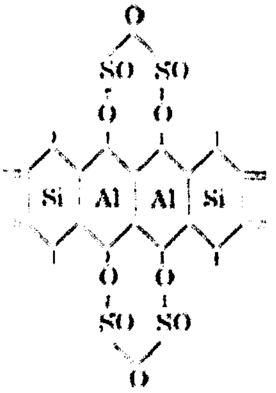
Most analyses of ultramarine have not been calculated into formulæ, and those which have been given often show wide differences between the calculated and ascertained values. This is considered, by most chemists, as being less due to errors in calculating the formulæ than to impurities in the material.

The calculation of these formulæ showed that ultramarines of the following types have already been prepared (see *Appendix*) :

1. $\hat{\bar{Si}} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}$,
2. $\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}$,
3. $\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \bar{Si}$,
4. $\hat{Si} \cdot \hat{Al} \cdot \hat{Si}$,
5. $\bar{Si} \cdot \hat{Al} \cdot \bar{Si}$.

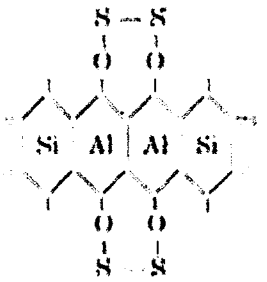
From type 1, for example, ultramarines of the following types have been produced :

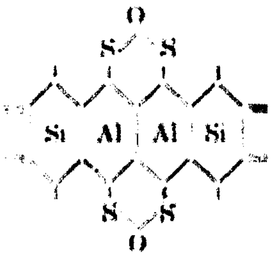




(a) $R_m(Si_{12}Al_{12}O_n)(S_2O_7)_2$.

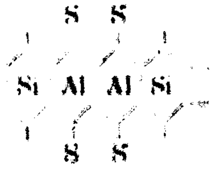
(b) $R_m(Si_{12}Al_{12}O_n)(S_2O_5)_2$.





(c) $R_m(Si_{12}Al_{12}O_n)(S_2O_2)_2$.

(d) $R_m(Si_{12}Al_{12}O_n)(S_2O)_2$.



(e) $R_m(Si_{12}Al_{12}O_n)(S_2)_2$.

Summary of Ultramarines obtained, arranged according to the foregoing Types

(a) $R_m(Si_{12}Al_{12}O_n)(S_2O_7)_2$.

1. $Na_{12}(Si_{12}Al_{12}O_{48})\cdot S_4O_{14}$.

(b) $R_m(Si_{12}Al_{12}O_n)\cdot S_4O_{10}$.

2. $Na_{11\cdot 5}K_{6\cdot 5}(Si_{12}Al_{12}O_{48})\cdot S_4O_{10}\cdot ONa_2$.
3. $Ag_{16}(Si_{12}Al_{12}O_{48})\cdot S_4O_{10}\cdot ONa_2(H_2O)_4$.
4. $Pb_8(Si_{12}Al_{12}O_{48})\cdot S_4O_{10}\cdot ONa_2(H_2O)_8$.
5. $Zn_8(Si_{12}Al_{12}O_{48})\cdot S_4O_{10}\cdot ONa_2(H_2O)_{16}$.

6. $Ag_{12}(Si_{12}Al_{12}O_{46}) \cdot S_5O_9 \cdot OAgNa$,
7. $Ag_{15}Na(Si_{12}Al_{12}O_{48}) \cdot S_5O_9$,
8. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_6O_8$.

(*c*) $R_m(Si_{12}Al_{12}O_n) \cdot S_4O_4$.

9. $Na_{16}(Si_{12}Al_{12}O_{48}) \cdot S_4O_4(H_2O)_2$,
10. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_5O_3 \cdot ONa_2$.

(*d*) $R_m(Si_{12}Al_{12}O_n) \cdot S_4O_2$.

11. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_4O_2$,
12. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_4O_2 \cdot Na_2$,
13. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_4O_2 \cdot Na_4$,
14. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_4O_2 \cdot Ag_4$,
15. $Na_6Ag_6(Si_{12}Al_{12}O_{46}) \cdot S_4O_2 \cdot Ag_4$.

(*e*) $R_m(Si_{12}Al_{12}O_n) \cdot S_4$.

16. $Na_{11 \cdot 5}K_{0 \cdot 5}(Si_{12}Al_{12}O_{46}) \cdot S_4Na_2$,
17. $Na_{16}(Si_{12}Al_{12}O_{48}) \cdot S_4Na_2$,
18. $Na_{12}(Si_{12}Al_{12}O_{46}) \cdot S_4Na_4$.

Ultramarines of other types are arranged according to their sulphonates.

The following additional pigments have been produced :

(*a*) $R_m(Al_pSi_rO_n) \cdot S_4O_{14}$.

19. $Na_{14}(Si_{16}Al_{12}O_{55}) \cdot S_9O_9$,
20. $Na_{16}(Si_{16}Al_{12}O_{56}) \cdot S_9O_9$,
21. $Na_4(Si_{12}Al_6O_{34}) \cdot S_6O_3 \cdot ONa_2$,
22. $Na_6(Si_{10}Al_6O_{31}) \cdot S_6O_3$.

(*b*) $R_m(Al_pSi_rO_n) \cdot S_4O_{10}$.

23. $Na_{16}(Si_{16}Al_{12}O_{56}) \cdot S_{10}O_4 \cdot O_2Na_4$.

(*c*) $R_m(Al_pSi_rO_n) \cdot S_4O_8$.

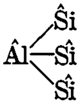
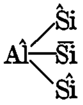
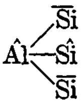
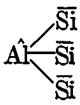
24. $Na_{14}(Si_{18}Al_{12}O_{59}) \cdot S_{12}$,
25. $Na_{18}(Si_{18}Al_{12}O_{61}) \cdot S_{12}$,
26. $Na_{20}(Si_{18}Al_{12}O_{62}) \cdot S_{12}$.
27. $Na_{12}(Si_{16}Al_{12}O_{56}) \cdot S_{12}$.

(*d*) $R_m(Al_pSi_rO_n) \cdot S_4O_2$.

28. $Na_8(Si_{12}Al_6O_{36}) \cdot S_6$,
29. $Na_{16}(Si_{18}Al_{12}O_{60}) \cdot S_6$,
30. $Na_{18}(Si_{18}Al_{12}O_{61}) \cdot S_5O$.

The above ultramarines exist both theoretically and actually. Other corresponding compounds must be produced sooner or later.

If the views just expressed with regard to the constitution of ultramarines are correct, these substances can only be produced from hydro-aluminosilicates with *a*-hydroxyls, and *not* from acids of the following types :

1.  2.  3.  and 4. 

as the latter contain no *a*-hydroxyls.

Ultramarines of these latter types are, as yet, unknown, and any attempts to produce them must prove abortive if the hexite-pentite theory is correct.

C

Many ultramarines of the greatest diversity of colour are in agreement with the theory. Thus :

1. According to Zeltner[229], violet ultramarine may be obtained from the blue or green varieties if chlorine or other halogen and hydrogen is passed through the given ultramarine at 160–180°, NaCl being separated.

2. According to Hoffmann[230], a purple-red or violet pigment may be obtained from blue or green ultramarine by treatment with acids or salts and air at a high temperature. A separation of the base—also probably of the sulphonate group—occurs.

3. J. Phillipp[231] obtained a blue ultramarine by treating green ultramarine with water at 160°, and concluded that sodium sulphide was liberated in the process.

4. Gmelin[232] had previously shown that blue ultramarine, when heated in a current of hydrogen, is converted into red ultramarine with the liberation of H_2S.

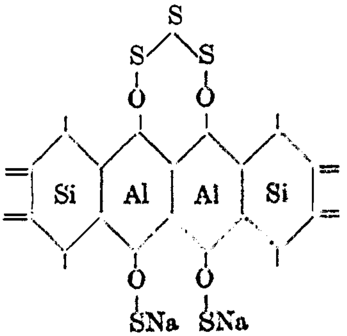
5. In the following compounds, with the same chromophore and the same silicate nucleus, but with a variable proportion of base, the deepening of the colour with increasing molecular weight—in accordance with Nietzki's law (p. 142)—is readily observable.

$Na_{14}(Si_{18}Al_{12}O_{59})S_{12}$ is red,
$Na_{18}(Si_{18}Al_{12}O_{61})S_{12}$,, violet, and
$Na_{20}(Si_{18}Al_{12}O_{62})S_{12}$,, blue.

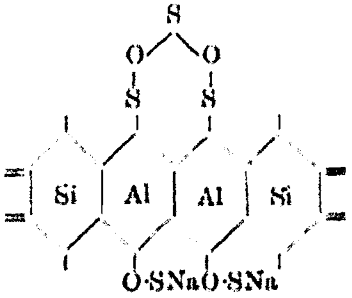
The possible existence of isomeric ultramarines follows naturally from the theory. Thus, there are four possible isomers for a compound with the formula :

$$Na_{12}(Si_{12}Al_{12}O_{46})S_{6}O_{4}Na_{2},$$

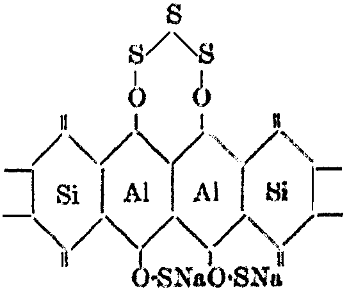
as may be seen from the following structural formulæ :



1.



2.



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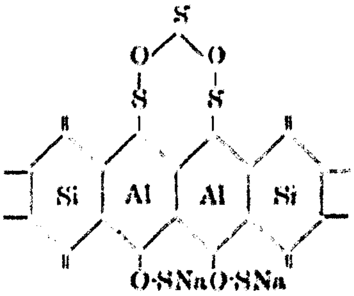


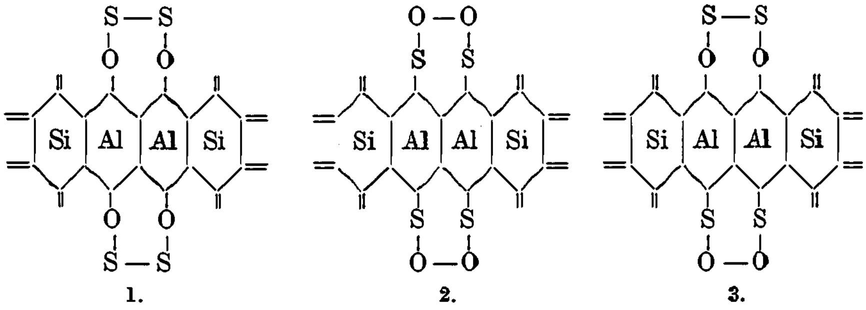
4.

The results of a number of analyses by R. Hoffmann[233], Heumann[234], and Phillipp[235] agree with the last-mentioned formula. In spite of the fact that all the ultramarines examined by these investigators had the same composition, they varied in their characteristics, the ultramarines of Hoffmann and Heumann being blue and that of Phillipp, green. Hence at least two isomers, out of those possible, are known.

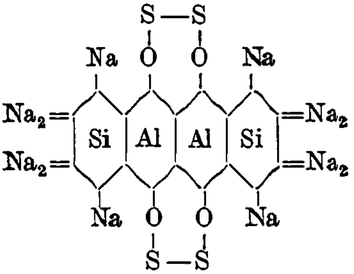
Further studies of these pigments must eventually lead to the discovery of new isomers, the composition of which can be predicted. Thus, there are *three* possible isomers of the compound

$$Na_{16}(Si_{12}Al_{12}O_{48}) \cdot S_{4}O_{4},$$

with the following structural formulæ :



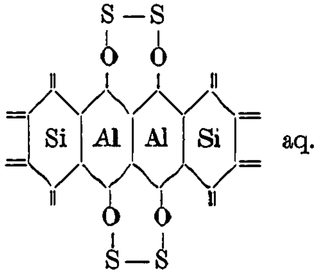
On treating a given ultramarine with an aqueous solution of a salt, e.g. the compound



with $BaCl_2$, $SrCl_2$, $ZnSO_4$, $AgNO_3$, etc., a substitution of the sodium by barium, strontium, zinc or silver, etc. may occur or the sulphonate group may pass into the new compound. The sulphonates, as already mentioned, are very labile radicles and can easily unite with or throw off oxygen, so that it is by no means impossible that the sulphonate of a new compound may be either rich or poor in oxygen.

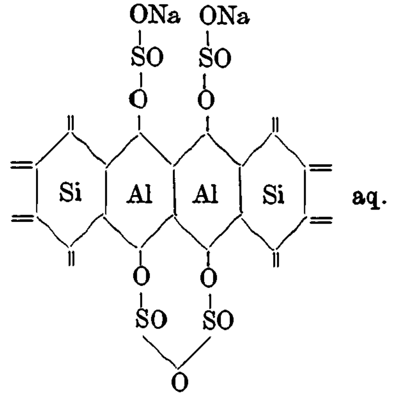
Szilasi[236] and Heumann[237] have reached the same conclusion in their investigation of the behaviour of ultramarine compounds and solutions of salts. Szilasi studied the behaviour of three green ultramarines (see *Appendix*)—one made at Budapest and the two others at Nuremberg. As it happened, all three samples had the same composition, viz. :

A.



$Na_{16}(Si_{12}Al_{12}O_{48}) \cdot S_4O_4(H_2O)_2$.

By treating this compound with a solution of $AgNO_3$, $Pb(NO_3)_2$ and $ZnSO_4$, Szilasi obtained the following ultramarines :

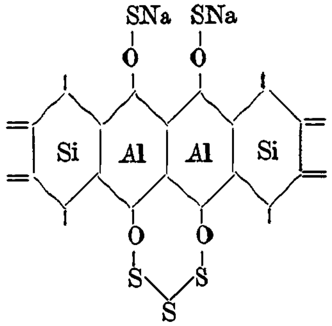
B. 

1. $Ag_{16}(Si_{12}Al_{12}O_{48}) \cdot S_4O_{10}ONa_2(H_2O)_4$,
2. $Pb_8(Si_{12}Al_{12}O_{48}) \cdot S_4O_{10}ONa_2(H_2O)_8$,
3. $Zn_8(Si_{12}Al_{12}O_{48}) \cdot S_4O_{10}ONa_2(H_2O)_{16}$.

The mode of formation of compound B from A is easily seen. On the silicate side there is a replacement of sodium by Ag, Pb or Zn, whilst one sulphonate has added oxygen and the other oxygen and Na_2O. The addition of Na_2O is due to the fact—noted by several investigators—that sodium ultramarines, on treatment with water, lose part of their sodium in the form of caustic soda.

That the sulphonates can lose oxygen and Na_2O in aqueous solution is shown by the fact that Szilasi was able to reproduce the original sodium salt A from the silver salt B 1, with the structural formula B, by treating the latter with sodium iodide.

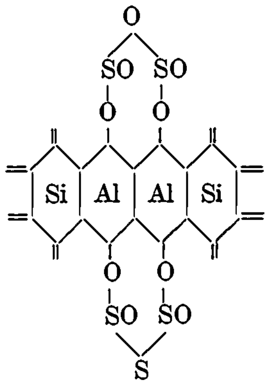
Heumann examined a blue ultramarine from Marienberg, the analysis of which (see *Appendix*, Analysis No. 10) corresponds to the formula :

C. 

$Na_{12}(Si_{12}Al_{12}O_{48}) \cdot Na_2S_5O_4$.

This sodium ultramarine was heated with silver nitrate in a sealed glass tube at 120° for seven hours and formed a yellow, silver ultramarine with a composition corresponding to :

D.



$Ag_{16}Na(Si_{12}Al_{12}O_{48}) \cdot S_5O_9$.

The sulphonate groups in this case were oxidised ; they added oxygen and lost Na_2O. The silicate side took up more base than compound C, as shown in formula D. Such cases have frequently been observed in the formation of complex silver and thallium salts (p. 19).

To all appearances, Heumann was able to reproduce the original sodium salt by heating the silver salt for eight hours at 130°–140° with a solution of sodium chloride, but, unfortunately, no analysis of this blue compound is available.

F

If the ultramarines are really derivatives of clays and are formed in the manner indicated by the hexite theory, the possibility of the formation at temperatures above the vitrification point of the clay must diminish with the amount of polymerisation which occurs and must cease entirely at the temperature at which the clay fuses, as at that temperature clays no longer contain α-hydroxyl. On the other hand, it must be possible to destroy the colour of any ultramarine by heating it to a sufficiently high temperature.

Knapp and Ebell[238] have shown that as soon as the temperature of an ultramarine reaches that of incipient vitrification, the possibility of its remaining blue diminishes and it ceases entirely at the fusion point of the material.

Gmelin[239] has shown that the colour of ultramarine may easily be destroyed by excessive or prolonged heating.

C. Stölzel[240] heated blue ultramarine to redness for a long time in a platinum crucible and noted that the colour gradually weakened and that a white product was finally obtained. A green ultramarine, when similarly heated, showed no diminution in colour. At first it darkened,

but then showed so great a stability that after several hours' "powerful heating" no further change could be noticed. In all probability, the vitrification point of the green ultramarine examined by Stölzel was above the "red heat" to which it was exposed; this accounts for the colour remaining unaffected. Further experiments will show whether the destruction of the colour of a number of ultramarines, which are stable at red heat, occurs at a higher temperature. According to the hexite theory, this must necessarily occur.

G

The separation of a sulphonate group in an ultramarine must result in a destruction of the colour. This is necessarily the case. Dilute acids, such as hydrochloric acid, effect a separation of the sulphonate group and produce a colourless mass.

H

If the ultramarines are real derivatives of clays, strong acids must not only effect a separation of the sulphonate groups, but must also affect the silicate nucleus and convert it into a compound of the most stable type, gelatinous silica usually separating out. No experiments in this direction are yet available. The truth of these conclusions—at at any rate as regards the separation of gelatinous silica—appears to be confirmed by Elsner[241], who treated two ultramarines—one blue and one green—with hydrochloric acid. Both lost their colour, sulphuretted hydrogen being evolved and gelatinous silica separated.

J

The authors' ultramarine theory gives a maximum content of monovalent bases in these substances. So far as the analyses studied by the authors are concerned, no ultramarine is known with a higher content of bases than the maximum shown by the hexite-pentite theory.

K

The theory also demands a minimum molecular weight for ultramarines. In this connection it is interesting to note that Guckelberger[242]—in studying the ratio $H_2S : S : SO_2$ in the decomposition of ultramarines by acids—has also arrived at the conclusion that the molecular weight of "ultramarine blue" is greater than that of an atomic complex with 6 silicon atoms, and that it is a multiple of Si_6. This view agrees with the theory proposed by the authors of the present volume.

L

It also follows from the theory, that the sulphonates form definite chemical compounds with silicate nuclei. Ritter[243] has reached the same conclusion experimentally. By the action of chlorine gas at

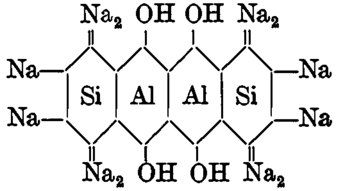
300° on the so-called white ultramarine, Ritter has shown that only a small quantity of sodium chloride is formed. From this he rightly concluded that, in the ultramarines, the sulphonates are in true chemical combination with the silicates, as any free sulphide compounds present would be completely decomposed by chlorine.

R. Hoffmann[244] is of the opinion that the sulphonate groups behave similarly to free sulphides, but are not quite the same as the latter as "they show a greater stability in the silicate compounds."

Analogy between Ultramarines and Sodalites

In concluding these observations, it is interesting to note the mode of formation of a number of compounds, the constitution of which is analogous to that of the ultramarines.

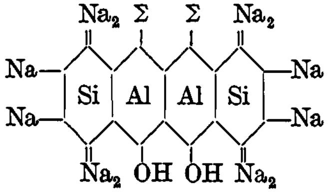
The assumption that some normal salts, e.g. Na_2SO_4, Na_2WO_4, $NaNO_3$, etc., contain "water of constitution," when in aqueous solution, is quite reasonable, as the formation of such hydrates is extremely probable (p. 267). If it is accepted, there is a possibility of forming compounds with these salts and an aluminosilicate corresponding to



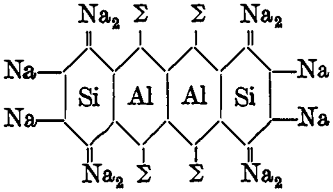
$$6\,Na_2O \cdot 2\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2.$$

A

If water is lost, the constitution of the resultant substances may be represented by the formulæ :



B



C

the sign Σ representing a molecule of a given salt (Na_2SO_4, Na_2WO_4, $NaNO_3$, etc.).

Thugutt (p. 60) has actually obtained a series of these compounds which may be termed "atomic compounds" (p. 59). From this atomic expression of the constitution of the sodalites it follows that a molecule of silicate *A* can combine with, at most, 4 molecules of Σ. This Consequence of the theory is confirmed by the facts, and no sodalite is

yet known which contains more than 4 molecules of Σ to one of A (see the series of Thugutt's sodalites on p. 60).

Theoretically it is also possible that the aluminosilicate A and other aluminosilicates with a-hydroxyls may not only combine with simple compounds and salts of the kinds mentioned—conveniently termed A (acid-) and Σ (salt-) sodalites—but also with complex acids and their salts.

The formation of sodalites (A- and Σ-sodalites) of the latter kind occurs in the so-called porcelain cements (p. 215).

Thugutt's sodalites and the porcelain cement sodalites may therefore be regarded as analogous to the ultramarines.

XIII

A New Theory of Hydraulic Binding Materials, with special reference to Portland Cement

The various substances known as " Portland cement " form only one division of the so-called hydraulic binding materials, the others being known as trass, puzzolans, hydraulic limes, Roman cement, slag cements, etc. Of all these, the Portland cements are the most important and valuable hydraulites.* Like the ultramarines, innumerable theories have been proposed to explain their chemical nature, but none of these theories is completely satisfactory.

If, as may be taken for granted, the solution of the problem is to be found in the chemical nature of the silicate cements and in the chemical constitution of the substances (silicates) from which they are derived, any attempt to apply the new hexite-pentite theory to the constitution of these cements must be of exceptional interest. If the new theory should prove to be of general applicability to the silicate cements it would not only solve one of the most interesting problems of inorganic chemistry, but the fact that it could afford such a solution would be of enormous value to the new theory itself.

Before endeavouring to apply the new theory to the hydraulic binding materials, it is desirable to review briefly and critically the various theories now in existence concerning cement, and to state in some detail the nature of the problem the solutions to which hitherto suggested have proved so unsatisfactory.

Historical and Critical Notes on previous Theories relating to Cements

The artificial production of Portland cement had scarcely been discovered when a question arose as to the cause of hardening † of

* A hydraulite is a substance which, when mixed with water to form a stiff paste, sets and becomes hard like a cement.—A. B. S.

† In English-speaking countries the " setting " and " hardening " of cements are treated as distinct. In the present volume, the term " hardening " is used to include all the processes which occur from the time the soft material, made by mixing the cement with water, begins to set to the time when the mass attains its maximum hardness.—A. B. S.

cements generally. A French engineer, Vicat[270], who had paid much attention to cements, set to work to investigate, and eventually concluded that the hardening was due to the combination of the cement with water. A closer investigation showed that there are several difficulties in the way of accepting this hypothesis, some substances, which were known to combine with water, never hardening like cement. Thus, the zeolites are hydrous aluminosilicates which, after being deprived of water, can absorb it again from the air, though, as Fuchs has shown, such dehydrated zeolites do not harden under water. Again, quicklime is well known to combine with water, yet the combination does not produce a hard, solid mass, but only a soft, friable powder. Fuchs[271] therefore sought for another explanation of the cause of the hardening, and eventually made the remarkable discovery —since repeatedly confirmed—that only those aluminosilicates which, on treatment with acids, produce gelatinous silica, possess the property of hardening with lime and water. Fuchs concluded that hardening is a chemical process in which part of the lime and the "attackable," "soluble" silica unite, on burning, to form a calcium silicate. Indeed, Fuchs went so far as to state the composition of the silicate which he supposed was formed. As no facts in opposition to this theory were known, it was not only accepted readily, but was used to great advantage. Pettenkoffer[272]—an energetic supporter of this theory—even suggested that Fuchs had so completely solved the problem that no further investigation was necessary! Feichtinger[273], however, sought for experimental proofs of Fuchs' theory, and believed he had found it in the following fact: if the hardening is due to a combination of soluble silica and free lime, the mixture must lose soluble silica in proportion to the amount of hardening which has occurred. This fact he confirmed on several occasions.

Fuchs' theory was published before the discovery of Portland cement, and, when applied to the latter, difficulties at once arose. One of these difficulties was that in Portland cement the chemical behaviour suggests that the whole of the lime is in a combined state and that no free lime is present to combine with the soluble silica. This was one of the first facts observed to be opposed to Fuchs' theory. Winkler[274] then found it necessary to devise a new theory for these hydraulites,* and at once assumed that in the newer cements the hardening was not so much the result of a new compound of lime and silica as of the separation of lime from a compound previously formed. He retained Fuchs' theory for silicate cements containing free lime (Roman cements) and concluded that in Portland cements the liberation of lime occurred until the same calcium silicate was obtained as Fuchs had found to be necessary in the other hydraulites.

Feichtinger[275], on the contrary, opposed Winkler's theory, and maintained that Portland cements contain free lime; to this extent he

* See the first footnote on the previous page.

supported Fuchs' theory. Nevertheless, it is possible to draw precisely the opposite conclusions from Feichtinger's experiments, i.e. the absence of free lime in Portland cement. He endeavoured to explain the inconsistency of his theory with the facts by means of a new and improbable hypothesis, viz. that the particles of free lime are so coated over with molten cement that a considerable amount of time is needed before the presence of the free lime becomes noticeable. Feichtinger examined various kinds of hydraulic limes, including those, like Portland cement, in which the whole of the lime is chemically combined, and those, like Roman cements, which contain free lime. Both are readily distinguished by their behaviour towards water; the former, on hydration, show a scarcely noticeable rise in temperature, whilst the latter show an unmistakable development of heat. Furthermore, Portland cements after a given period of hydration show no $Ca(OH)_2$, whilst in the Roman cements this substance may be detected as soon as water is added. This is in direct contradiction to Fuchs' theory. In order to retain this theory, Feichtinger had recourse to the improbable hypothesis mentioned above.

Winkler[276] has argued that the behaviour of Portland cement towards an alcoholic solution of phenolphthaleïn shows that the whole of the lime is in a chemically combined state, as the smallest trace of free lime would, if present, turn the indicator red. In reality, no such red colour is produced. Fuchs' theory is inconsistent with the possibility of regenerating the cement from the set or hardened mass, though this possibility may be inferred from Feichtinger's experiments, as will be shown later. No agreement was ever reached by Feichtinger and Winkler: each retaining his own opinion to the last. This shows how strong was the influence of Fuchs' theory on Feichtinger.

No absolute answer to the question, "Does Portland cement contain free lime?" has been given, even at the present time; the influence of Fuchs' theory has been so strong.

It is also interesting to note how the supporters of the "free lime" hypothesis endeavoured to disparage the value of the phenolphthaleïn reaction. Some of them suggested that the "free" lime in Portland cement is in a crystalline state and so is incapable of reaction as an alkali. This suggestion is futile, as Richter[277] has prepared crystallised lime and has shown that in alcoholic solution it has an obvious alkaline reaction.

Fremy[278] endeavoured to show the presence of free lime by treating Portland cement with dilute acids, but Schuljatschenko[279] has rightly shown that the behaviour of Portland cements towards dilute acids is a most unsatisfactory premise on which to argue for the presence of free lime, as the whole of the lime present can be removed from the cements by means of dilute acids.

Other investigators have used other reagents[278] * such as $Mg(NO_3)_2$.

* A list of reagents which have been tried for showing the presence or absence of free lime in cement will be found in the Bibliography under No. 278.

A considerable replacement of lime then occurs, and has been considered to prove that Portland cement contains free lime. That this conclusion is false may be readily understood when it is remembered that such reagents are precisely those which decompose the cement. Michaelis[280] has rightly shown that the ease with which lime may be liberated by the action of certain reagents does not prove that a portion of the lime in Portland cement is in a weaker state of combination. The statement made by Hardt[281], that "feebly combined lime" is the same as "free lime," is also quite erroneous.

Nor does it follow that soluble silica plays a special part in the hardening of cement, even though it is true that only those silicates which contain "soluble silica" are hydraulic. Erroneous ideas as to the part played by "soluble silica" occur throughout the literature of cement ever since the time of Fuchs, and have, hitherto, rendered it impossible to evolve a sufficiently comprehensive theory of hydraulites. Many hydraulites, such as plaster, lime-aluminates, lime-borates and several calcium and magnesium oxides, contain no silica at all. Is it not probable that these silica-free substances harden in accordance with the same general law as the silicate cements? Yet no one appears to have realised the possibility of the "soluble silica" taking no part whatever in the hardening process, for even Jordis and Kanter[282], who regard all previous theories respecting the constitution of cements as without foundation and erroneous, lay great emphasis on the importance of "soluble silica" in the hardening of cement.

The influence of Fuchs' theory is also shown by Heldt[283], who was clearly of the opinion that the value of cements lies chiefly in the proportion of "soluble silica" they contain and that the alumina is only detrimental, when he wrote: "If an aluminosilicate is present in a mortar (cement) it exists simply as a wholly inert material and takes no part in the setting or hardening, but is harmful because it reduces the proportion of silica present. Each per cent. of aluminosilicate which is not combined with lime is lost, so far as the formation of a hardening compound is concerned, and remains as an insoluble and inert material." It is not surprising that Heldt drew the following curious inference from this theory: "If it were possible to prepare a hydraulic mortar (cement) containing 23 per cent. of soluble silica, all existing cement works would be ruined, as the best Portland cement only contains 15-16 per cent. of soluble silica, which is reduced, by the addition of water and after hardening, to only 7 to 10 per cent. in the final product."

Chatoney and Rivot[284]—two French investigators—endeavoured to put Heldt's theory to practical use. Schuljatschenko has published the following comments on this interesting portion of the history of the cement industry: "Two writers, Chatoney and Rivot[284], the latter a learned chemist and professor at the School of Mines, in their treatise on materials employed in structural work on the sea coast,

reached the remarkable conclusion that only those cements are durable in sea-water which consist of the simplest compounds such as those made of lime and silica. Roman cements, puzzolans and other cements lack durability in so far as their composition is complex. . . ." These authors arranged that the sea walls in the harbours of St. Malo and La Rochelle should be built with silicates free from alumina, and it is easy to understand the panic which occurred among French engineers when they noticed the rapidity with which the cement used at these places was destroyed.

Fuchs' theory also influenced the methods of investigation of the constitution and hardening of Portland cements. His view, that the hardening was due to the formation of a given calcium silicate, led to an enquiry as to which substances were formed during the hardening of the cement. These substances were later termed the "effective substances" of the cement. For over fifty years innumerable investigators have endeavoured to find the substance which is the chief cause of the hardening of cements,* and it is noteworthy that everyone who was able to prepare an aluminate or silicate which possessed the power of setting in water, at once declared that it was to this substance that Portland cement owes its setting power! The result is that there are nearly as many "effective substances" as investigators. All kinds of calcium silicates—from the mono- to the hexa-silicates—and many calcium aluminates have been prepared in this connection, and, to add to the difficulty, the silicates which one investigator declared to be hydraulic were found by another to have no hardening power. "Hence, almost all possible calcium silicates," write Jordis and Kanter[284b], "have been 'found' in cement clinker; indeed, some investigators have not confined themselves within the limits of the theoretically possible! There is, in fact, a repletion of silicates calculated from cement analyses, the only evidence for the existence of which is that the (assumed) compositions of these various silicates, aluminates, ferrates, etc., when added together in the proportions in which they are alleged to be present, agree with those of Portland cement. Surely this is a weak argument when it is realised what is meant by the inclusion of all the possible combinations!"

Fuchs' theory is also responsible for the fact that no one has hitherto regarded the Portland cements as chemical compounds, as this would be in direct opposition to the view that the value of a cement lies in the (free) "soluble silica" present. It has, in fact, been generally agreed that Portland cement is either a mixture of various compounds (*cf.* the theories of Le Chatelier[285], the Brothers Newberry[286], Kosmann[287], Jex[288], etc.) or a fused mass of indefinable compounds. Erdmenger[289] regards Portland cement as a "glass"; Hardt[290] as a "solid solution," and the theories propounded by Schönaich-Carolath[291], Schott[292], Zsigmondy[293], Meyer-Mahlstatt[294], Rohland[295], etc.,

* For a list of theories of hardening the reader should refer to No. 284a in the Bibliography.

are of a similar nature.* These theories find a merely superficial support from the microscopical examinations of thin sections of clinker by Le Chatelier[296], Feret, Törnebohm[297] and others, who have found that commercially valuable clinker may be composed of several different materials.† Törnebohm[297] has suggested the terms "*alite*," "*belite*," "*celite*," and "*felite*" for the chief of these constituents.

This suggestion—although at first sight it appears to be in support of a "mixture" theory—is not at all determinative, for no one has yet been able to isolate these various constituents (e.g. by means of a mechanical analysis), nor is there any general agreement as to the composition of these "constituents." Thus, Le Chatelier considers that the clinker is chiefly composed of tri-calcium silicate—a substance which has not yet been prepared, with certainty, in a crystalline state, but is a purely hypothetical one. Törnebohm, on the contrary, regards it as a product composed of alumina, silica, and calcium.

If *alite*, *belite*, etc. exist as real constituents of cement, each having a different composition, it must be impossible to obtain cement clinker of perfect uniformity. Yet Richardson[299] has produced clinkers which, when viewed in thin sections, appear to be completely homogeneous, and correspond exactly to good commercial clinkers.‡

It is very probable that the want of uniformity observed by Le Chatelier, Törnebohm and others in thin sections of clinker, is due to a crystallographic and not to chemical differences in the material. This appears all the more probable when it is remembered that it has not yet been found possible to isolate any definitely characteristic constituents from the clinker by means of sedimentation or mechanical analysis. For instance, Schott[299] found that a mechanical separation by means of moving fluid merely divided the material into grains of different sizes, the finest having the same chemical composition as the coarsest.

[The preparation of transparent sections of cement, as mentioned above, is extremely difficult and is not altogether satisfactory. It is much better to make a micrographic analysis of pieces of polished cement clinker etched with water or 1 per cent. hydrochloric acid and viewed by reflected light. Such pieces show that the greater part of the cement is composed of crystals of a single constituent ("*alite*"), separated by a much smaller quantity of intercrystalline material (*celite*? with traces of *belite*?). Only the crystalline matter is of value, the other being quite inert. The composition of the intercrystalline matter is uncertain; it may be the same as that of crystals, the material being merely in a different physical state.

Pure "*alite*" has been prepared by O. Schmidt and K. Unger (*Der Portland*

* For further information on the constitution of cement clinkers see No. 295 in the Bibliography.

† For further information on the microscopical examination of cement see No. 298 in the Bibliography.

‡ In a *critique* of the hexite-pentite theory made shortly after the publication of the German edition of the present work, Allen and Shepherd stated that a reinvestigation of Richardson's clinkers with improved appliances showed that they were not homogeneous. This discovery, which was not known to the authors when this book was written, does not affect their argument, but only shows that Richardson was unable to produce, as he had hoped, a perfectly homogeneous cement. This has, however, been obtained by Schmidt and Unger, as pointed out in the translator's note (below).

Zement, Stuttgart, 1906, p. 102) by heating a mixture containing 67 per cent. of lime to fusion. The "*alite*" crystals had a composition corresponding to:

Limo	67.33
Silica	23.50
Alumina	3.82
Iron oxide	2.28
Magnesia	2.34
Other matter	0.73
	100.00

According to C. Desch[709], "These crystals are completely homogeneous, so that we are fully justified in regarding them as a solid solution of calcium silicate and aluminate, but not in assigning to them a definite chemical formula."

This statement of Desch's is most peculiar. Surely the fact that the material is crystalline is opposed to its being a "solid solution," and in any case it is not clear why it is wrong to assign a chemical formula to crystals.

In criticising the German edition of the present work, C. Desch complains that the authors have not paid sufficient attention to the structure of cements as revealed by the microscope. Yet this investigator, whilst accepting the homogeneity of Schmidt and Unger's cement, refuses to regard it as a definite chemical compound! The "solid solution" theory, which he prefers, has been exhaustively discussed in the general criticism of the various theories respecting silicates (p. 13) and is further confuted by the fact that no Portland cement has yet been found which does not conform to the hexite-pentite theory, which states that such cements are highly basic calcium salts of aluminosilicic acids. Besides, the properties of Portland cement do not coincide with Desch's or any other theory of mixed crystals. (*Vide* pp. 13, 22 and 162.) In short, there can be no single substance forming the essential constituent of all Portland cements and corresponding to *alite*, because, as the authors' formulae show, the compositions of cements differ greatly from each other, although they all admittedly fall within certain limits when expressed in the form of an ultimate analysis.]

There is a sense in which all theories published on the silicate cements are developments of that of Fuchs, and a considerable number of investigators at the present time are still under its influence. It is, however, impossible to find that these theories have led to any satisfactory results, but rather to the opposite. The worthlessness of these theories is particularly noticeable when an attempt is made to use them in explaining the various experimental results which have been obtained in silicate cements. Thus, in the light of the foregoing theories, the following facts are inexplicable:

(*a*) It is known that the best temperature for burning a mixture of clay and lime or chalk in the production of Portland cement is the temperature at which the amount of vitrification is readily appreciable to the unaided eye * and that the quality of the cement also depends on the duration of the heating. If this is too prolonged or the temperature is too high, a cement of lesser, or of insignificant value is produced.

The theories previously mentioned afford no explanation of this important fact.

(*b*) Silica cements which have been heated to the sintering point, become gelatinous when treated with dilute acids.

This fact is well known, but not the slightest explanation has yet been given as to its cause.

* This is sometimes termed the "sintering point." It is reached when sufficient fusion has occurred to render the mass impervious to any suitable fluid which has no chemical action on the material.—A. B. S.

(*c*) It is known that in Portland cements a portion of the lime is more readily removable than the remainder. The usual explanations offered are that cements contain both free and combined lime, or that part of the lime is in a state of weaker combination than the rest. The first or "free lime" hypothesis has been shown in previous pages to be opposed to the facts. The second is often thought to be supported by the supposed presence of highly basic silicates and aluminates in the cement. The behaviour of Portland cement towards certain reagents is, however, opposed to this hypothesis. The supposition that calcium silicates are present is founded on Winkler's experiments, which showed the calcium silicates to be insoluble in an alcoholic solution of hydrochloric acid. From this it was argued that those portions of cement which are insoluble in this reagent are composed of calcium silicate. Calcium aluminates react alkaline to an alcoholic solution of phenolphthalein. Portland cements should, therefore, produce a red colour with this reagent. As a matter of fact, they do not do so.

Hence, the ready separation of a definite proportion of lime from Portland cements is very puzzling in the light of previous theories.

(*d*) By granulating furnace slags it has been found possible to produce silicate cements which will only set or harden in the presence of water containing lime or other alkalies in solution. None of the theories previously mentioned can be used to explain this fact. According to Zulkowski[300] some Portland cements, as soon as they have lost a certain percentage of lime, possess this characteristic of slag cements and will only harden in the presence of alkaline fluids and not at all with water alone. None of the existent theories show any genetic relationship between the Portland cements and the slag cements.

As a matter of fact, there is such a relationship, as will be shown later.

(*e*) Lunge's[301] investigations on the resistance to alkalies of granulated and ungranulated slags showed that, in the latter, the aluminium is more strongly combined than in the former. There is no explanation of this fact outside the present volume.

(*f*) The existing theories neither permit the prediction of the following facts, nor do they provide a satisfactory explanation of them:

(1) According to Schott[302] a considerable proportion of lime may be removed from a cement without affecting its setting and hardening power.

(2) According to Michaelis[303], Schott, and others, it is possible to reproduce the original cement from one which has been fully hardened.

(3) If a cement is allowed to set and is then ground to powder and again mixed with water, it will again set hard, but not so strong as before.

(*g*) There can be scarcely any doubt that hardened cements are very sensitive to certain salts, particularly to sulphates. None of the existing theories can explain this harmful action of sulphates, nor do they indicate any means whereby it may be avoided. When it is remembered that an explanation of the harmful action of sulphates on cement is probably the most likely means of overcoming the difficulties caused by these compounds—including the possible solution of the rea-

water problem—it is not difficult to imagine that the inability of existing theories to throw any light on this important subject is one of the gravest objections to their use. Another special weakness of existing theories lies in the assumption made in almost all of them, that Portland cements are not single compounds. This assumption, which is entirely without foundation in fact, not only limits the development of chemical knowledge of the silicate cements, but makes such development quite impossible.

The opinion that Portland cements do not form chemical individuals is doubtless due to the prevalent ideas of the constitution of the substances from which these cements are derived, viz. the clays. The conception of other derivatives of clay, such as the ultramarines, as chemical individuals is also made difficult for the same reason.

Now that it has been shown (*a*) that the clays and ultramarines may be regarded as true chemical individuals (i.e. as definite chemical compounds), (*b*) that by so regarding them, the whole mass of published experiments on the silicates becomes explicable, and (*c*) that this conception of them has the characteristics of a true chemical theory—one which permits a single classification for all these substances as well as the deductive study of them—it appears to be highly probable that the Portland cements, which are nothing more than derivatives of clays, may also be regarded as chemical individuals, provided that no facts are opposed to this view.

When it is added that by thus regarding the Portland cements as definite chemical individuals and applying the new hexite-pentite theory to them, the meaning of the whole mass of published experimental results becomes clear and that a new means of solving the important "sea-water" problem is provided, it is hardly too much to suppose that there will scarcely be a chemist who will continue to regard Portland cements in the old erroneous manner as mixtures of various substances.

In applying the new theory to Portland cements, the following subjects must be considered :

(*a*) The chemical constitution of the Portland cements.

(*b*) The reactions which occur during the formation of Portland cements, and the influence of the duration of heating and of the temperature on the products.

(*c*) A new theory of setting and hardening.

At the suggestion of A. B. Searle the following statements, which occur in various text-books, are dealt with more specifically than in the original (German) edition of this treatise :

(*a*) The temperature in a cement kiln only effects a partial fusion of the material.

(*b*) Chemical reactions between solid substances take place very slowly and are seldom complete.

(*c*) Cement clinker is not a homogeneous substance, but merely a mixture or a solid solution, and correct conclusions as to its chemical constitution cannot be drawn without studying each of the constituents separately.

(*d*) The chemical reactions which occur in the burning of cement are never complete, and it is therefore incorrect to regard the product as a single compound, the constituents of which are in proportions conformable to the laws of Dalton and Proust.

(e) Cement clinker consists essentially of colloidal substances and the properties of cement are due to the colloidal nature of its various constituents.

With respect to (a), a partial fusion of the material is not incompatible with the unitary nature of the clinker, i.e. it does not necessarily imply that clinker is not composed of a single definite compound. The partiality of the fusion is due to the low heat conductivity of the material, whereby the melting point is not reached in the interior of the mass.

[An interesting parallel to this was found by J. W. Cobb, who showed that lime and silica enter into complete combination even though the temperature reached is far below that required to fuse the lime and silica or the compound so formed.]

The statement (b), that the chemical reactions between solid materials are slow and seldom complete, is by no means true at high temperatures. Besides, there is no positive proof that on heating a mixture of kaolin with calcium carbonate (the pure constituents of a raw cement mix) the clinker contains free clay as well as free calcium carbonate or rather free lime. On the contrary, the very small proportion of insoluble matter in cement clinker (only 1–2%) shows that the reaction is remarkably complete.

[Cobb's experiments, mentioned above, afford a further proof of the speed and completeness of reactions between solid substances.]

That, as stated in (c), clinker is a mixture and not a compound is purely an assumption and not a fact. Of the two assumptions, (1) that cement clinker is a compound, and (2) that it is a mixture, that must be the more probable which satisfies the most facts and enables the prediction of the most properties to be made. This is unquestionably true of the assumption that cement clinker is a true chemical compound.

Statement (d) is sufficiently answered in the comment on statement (b) given above.

Statement (e) that cement clinker is essentially colloidal is another pure assumption which is quite unnecessary. It is true that cements have some characteristics in common with colloids, especially with regard to their behaviour on treatment with water. Any confusion which may arise in this connection can only be due to a superficial appreciation of the properties and structure of colloids. For, as a matter of fact, the colloidal properties of cements and clays are by no means incompatible with their chemical individuality, and, in the authors' opinion, the colloids themselves are not mixtures, but definite chemical compounds of very high molecular weight.

It is most surprising that C. Desch, on the one side, and E. T. Allen and E. S. Shepherd, on the other, in their reviews of the German edition of this work reproached the authors of the H.P. theory for regarding Portland cements as definite chemical compounds and not as mixtures. These critics believe that the microscopical investigation of cements has shown positively that cements are heterogeneous substances. This is the sole argument which has been brought in opposition to the H.P. theory.

Unfortunately, these critics have omitted to bear a very important

fact in mind, namely, that a difference in crystal form does not necessarily prove the presence of substances of different chemical composition. There is always a great probability of di- or poly-morphism, whereby one and the same substance may assume different forms.

[The various forms which sulphur assumes is a particularly interesting example of polymorphism brought about by cooling under different conditions.]

A proof of the non-identity of the various crystalline substances in cement can only be furnished by proving that each of them has a different chemical composition. This proof—simple as it appears to be—is entirely wanting with regard to Portland cements, and all attempts which have so far been made to separate the various crystalline constituents have proved abortive.

These critics appear to adhere to one of the numerous mixture theories of the constitution of cements, and it would be of great interest if they would only state which is the one they prefer. If it were correct to speak of a " fog of theories " such a term might well be applied to the various mixture theories applied to Portland cements. Jordis and Kanter, in their well-known work on cements, have stated that all kinds of compounds, of possible and impossible theoretical constitution, may be present as essential constituents, and when enquiry is made as to what the various theories explain, it is almost impossible to find a simple answer. The following lines will give the reader a clearer idea as to the nature of the mixture theories :

Some writers state the composition of only a limited number of constituents ; others give the composition of the clinker. In the former class are Jex, Le Chatelier, Erdmenger, Rebuffat, Zulkowski, etc. ; in the latter are Kosmann, Newberry, Jex, etc.

The constituents of cement clinker according to the writers named below are shown in the following Table :

Alleged Constituent	Year	Authority Quoted and Reference
	1884	Le Chatelier, *Bull. de la Soc. Chim.*, 41, 377.
SiO_2	1900	Jex, *Tonind. Ztg.*, 1900, 1856.
$2\ CaO \cdot SiO_2$.	1893	Erdmenger, *Chem. Ztg.*, 1893, 982.
	1899	Rebuffat, *Gaz. Chim. ital.*, 28, II.
	1901	Zulkowski, *Chem. Industr.* 1901, 290, and Pamphlet, 1901.
	1901	Leduc, *Sur la dissociation des produits hydrauliques*, Sept., 1901.
$3\ CaO \cdot SiO_2$.	1856	Rivot & Chatoney, *Comptes rend*, 153, 302, and 785.
	1885	Le Chatelier, *Bull. de la Soc. Chim.*, 42, 82.
	1885	Spencer & Newberry, *Tonind. Ztg.*, 1898, 879.
	1901	A. Meyer, *Bull. Boucarest*, 1901, No. 6; *Tonind. Ztg.*, 1902, p. 1895.
	1901	Ludwig, *Tonind. Ztg.*, 1901, p. 2084.
	1902	Kosmann, *Tonind. Ztg.*, 1902, p. 1895.
	1902	Clifford Richardson, *Tonind. Ztg.*, 1902, p. 1928.
$2–3\ CaO \cdot SiO_2$.	1903	Michaelis, *Versammlung des Vereins der Portland Zement fabrikanten*, 1903.
$3–4\ CaO \cdot SiO_2$.	1856	Winkler, *Jour. f. prakt. Chemie*, 67, 444.
$5\ CaO \cdot 2\ SiO_2$.	1865	Heldt, *Jour. f. prakt. Chemie*, 94, 202–37.

The true composition of clinker is, according to Kosman (1895):

$$4\,Ca_2SiO_4 + \begin{Bmatrix} Ca_2 \cdot Al_2O \cdot O_4 \\ Ca_2 \cdot SiO_2 \end{Bmatrix},$$

According to Newberry (1898):

$$x\,(3\,CaO \cdot SiO_2) + y\,(2\,CaO \cdot Al_2O_3).$$

According to Jex (1900):

$$\begin{array}{ccccc} a\left({}^{Fe}_{Ca}[SiO_4]_2\right) & + & b\left({}^{Al_2}_{Ca}\Big\}(SiO_4)_2\right) & + & c(CaSiO_3) \\ | & & | & & | \\ | & & 2\,CaO & & | \\ | & & | & & 1\,CaO \\ 2\,CaO & & 8\,CaO & & \end{array}$$

and according to Ludwig (1901):

$$3.033\,CaO + 0.125\,MeO + 0.217\,Al_2O_3 + 1\,SiO_2,$$
$$\text{or } 3.158\,MeO + 0.217\,Al_2O_3 + 1\,SiO_2.$$

The published opinions as to the chemical composition of hardened cements and of the constituents which cause this hardening are equally divergent and confusing, as the examples in the following Table will show:

Alleged Constituents Causing the Hardening of Cements

Alleged Constituent	Authority Quoted and Reference
$CaO \cdot SiO_2 \cdot H_2O$	Le Chatelier, *Bull. de la Soc. Chim.*, 1885, 42, 82.
	Jex, *Tonind. Ztg.*, 1900, 1856-1919.
	A. Meyer, *Bull. Boucarest*, 1901, No. 6.
	Zulkowski, *Pamphlet*, 1901.
$4\,CaO \cdot 3\,SiO_2 \cdot H_2O$	Landrin, *Compt. rend.*, 1883, 96, 156, 379, 841, 1229.
$5\,CaO \cdot 3\,SiO_2 \cdot H_2O$	Michaelis, *Jour. f. prakt. Chemie.*, 1867, 100, 257-303.
$3\,CaO \cdot 2\,SiO_2 \cdot H_2O$	Michaelis, *Verhandlung d. Vereins z. Beförd. d. Gewerbefleizes*, 1896, 317.
$2\,CaO \cdot SiO_2 \cdot H_2O$	Rebuffat, *Tonind. Ztg.*, 1899, 782, 823, 853, 1900.
	A. Meyer, *Bull. Boucarest*, 1901, No. 6.
	Erdmenger, *Chem. Ztg.*, 1893, 982.
$3\,CaO \cdot SiO_2 \cdot H_2O$	Rivot & Chatoney, *Compt. rend.*, 1856, 153, 302, 785.
	Michaelis, *Jour. prakt. Chemie.*, 1867, 100, 257-303.

Michaelis has also stated that the composition of a fully hardened cement may be represented by:

$$246\,(3\,CaO \cdot R_2O_3 + 3\,H_2O) + 661\,(5\,CaO \cdot 3\,SiO_2 + 5\,H_2O) + 93\,(CaO + H_2O).$$

Allen and Shepherd have made the remarkable statement that the view that Portland cement is a mixture of various constituents is supported by 'a large amount of evidence.' It would be most interesting to see this voluminous evidence, as it is entirely unknown to the authors of the H.P. theory. Indeed, these critics appear to have overlooked

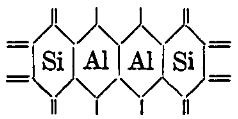
a fact to which Rohland has drawn attention, namely, the undeniable relationship between the constitution of clays, ultramarines and Portland cements. If Portland cements were mixtures, then clays and ultramarines could not be definite chemical compounds, yet the available experimental evidence is entirely in support of their definite chemical composition.

Almost all students of the constitution of Portland cements have overlooked the following considerations :

Portland cements are, theoretically, highly basic lime salts of aluminosilicic acids, i.e. they are basic salts of which clays are the corresponding acids. Their general properties are in entire agreement with this view of their constitution, and it is incomprehensible that on treating clay with calcium carbonate in the manufacture of cement, the product should not be a lime salt, but a mixture of various silicates and aluminates. It must also be remembered that Vernadsky has proved that free carbon dioxide is evolved when kaolin is heated with sodium carbonate and that a sodium salt is formed quantitatively. Analogous reactions occur in the synthesis of ultramarine from clay, sodium carbonate and sulphur, wherein sulphur addition-products of the sodium salt of the clay are formed. There is no foundation whatever for the assumption that the reaction between calcium carbonate and clay produces any other substances than those which the H.P. theory demands.

(*a*) The Chemical Constitution of the Portland Cements

If any suitable hydro-aluminosilicate such as



$$\overset{\circ}{H}_{20}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

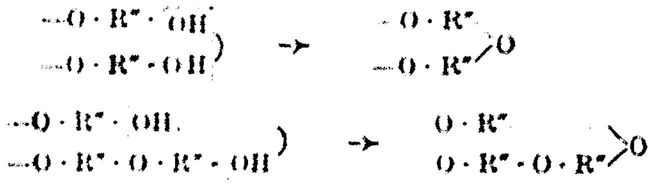
—which has been repeatedly mentioned on previous pages—be examined, it will be found (p. 139) to possess two kinds of OH-groups, viz. *a*- and *s*-hydroxyls. The *a*-hydroxyls play a special part in the formation of the *A*-aluminosilicates; in the formation of Portland cements the *s*-hydroxyls are specially important. The hydrogen of the *s*-hydroxyls—which may be briefly referred to as *s*-hydrogen—is, unlike the *a*-hydrogen of the *a*-hydroxyls, replaceable by such groups as :

$$—R'' \cdot OH, \quad —R'' \cdot O \cdot R'' \cdot OH \quad \text{and} \quad —R'' \cdot O \cdot R'' \cdot O \cdot R'' \cdot OH,$$
$$(R'' = Ba, Sr, Ca, Mg, \text{etc.})$$

The basic atomic complexes are known as hydro-basic groups and as side-chains.* If the elements of water are split off from two neighbour-

* For an explanation of side-chains a good text-book on organic chemistry should be consulted.—A. B. S.

ing (*ortho*) positions in the hydrobasic side-chains, anhydrobasic groups are formed as shown :



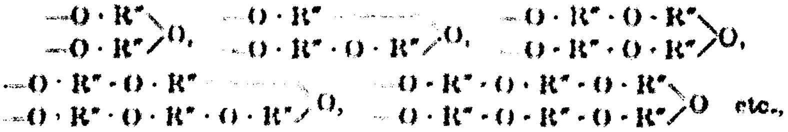
The hydrobasic atomic complexes

$-O\cdot R''\cdot OH$, $-O\cdot R''\cdot O\cdot R''\cdot OH$ and $-O\cdot R''\cdot O\cdot R''\cdot O\cdot R''\cdot OH$

may be represented, according to the number of R″-atoms, by

(1), (2) and (3),

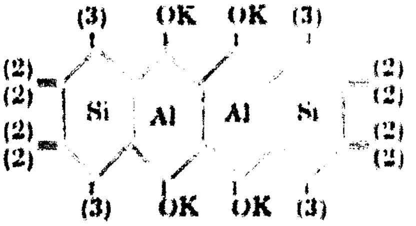
respectively, and the anhydrobasic complexes



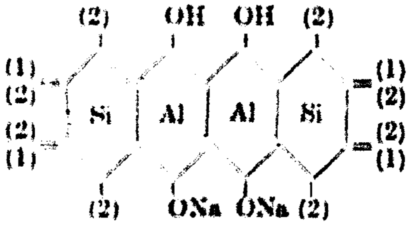
may each be indicated, according to the number of R″-atoms, by

2°, 3°, 4°, 5°, 6°, etc.

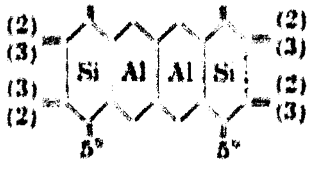
A few examples will make this clear :



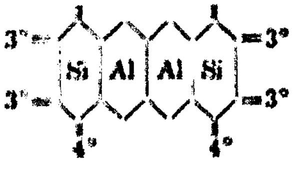
$2\,K_2O\cdot 28\,R''O\cdot 6\,H_2O\cdot$
$6\,Al_2O_3\cdot 12\,SiO_2$
Hydrobasic Salt.



$Na_2O\cdot 20\,R''O\cdot 6\,H_2O\cdot$
$H_2O\cdot 6\,Al_2O_3\cdot 12\,SiO_2$
Hydrobasic Salt.

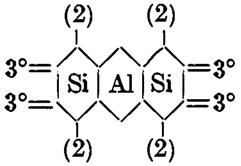


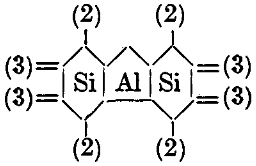
$4\,H_2O\cdot 40\,R''O\cdot 6\,Al_2O_3\cdot 12\,SiO_2$
Hydro-anhydrobasic Salt.

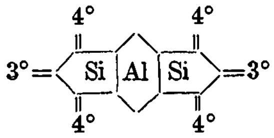


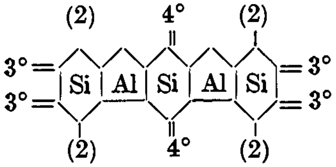
$28\,R''O\cdot 6\,Al_2O_3\cdot 12\,SiO_2$
Anhydrobasic Salt.

What has been stated with regard to substances of the type $\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}$ is equally applicable to other types, and the existence is, therefore, possible of :









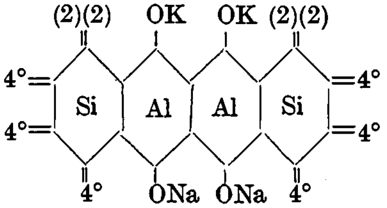
etc. etc.

The Al may be partially or completely replaced by the sesquioxides Fe‴, Cr‴, Mn‴, Ce‴, etc., and the Si by Sn, Ti, Zr, etc., whereby the number of these basic salts is largely increased.

Some of these basic salts with definite hydro- or anhydro-basic side-chains (viz. when R″=Ca, Mg) are manufactured on a large scale and are sold commercially in a finely-powdered state under the name of "Portland Cement." (It would be more correct to use the plural form —"Portland Cements.")

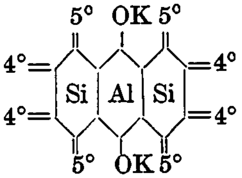
These Portland cements certainly contain 3° chains ; their maximum content of base remains to be found. Good samples appear never to exceed a maximum corresponding to 6° side-chains. Apart from this, these cements appear to contain a little alkali (in the aluminium hexite), a little water (probably basic), and small quantities of such salts as K_2SO_4, K_2CO_3, Na_2SO_4, $CaSO_4$, etc., but only as impurities.

The following are typical examples of Portland cements :



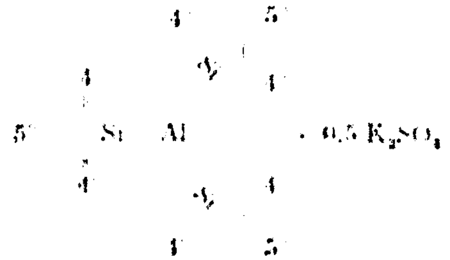
$\underbrace{+ 0.5\ CaSO_4 + 0.5\ Na(K)CO_3}_{\Sigma}$

$2\ H_2O \cdot 24\ CaO \cdot 8\ MgO \cdot K_2O \cdot Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 + \Sigma.$



$+ 0.5\ NaCl$

$20\ CaO \cdot 16\ MgO \cdot K_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 + 0.5\ NaCl.$



$39\ CaO \cdot 3\ Al_2O_3 \cdot 15\ SiO_2 \cdot 0.5\ K_2SO_4$. etc. etc.

(b) The Reactions occurring in the formation of Portland Cements, and the influence of the time of heating and the temperature on the Products

Portland cements may be made by burning the most widely different clays with definite quantities of lime or calcium carbonate. The ratio of lime to clay naturally varies with the latter. Hitherto, the proportion of lime and clay has been fixed empirically, i.e. it has been arranged according to a definite rule (termed the *hydraulic modulus*) for each kind of clay.

As, according to the authors' theory (p. 102), the clays are merely aluminosilicic acids, the reactions which occur in the burning of cement are obvious, and consist chiefly in replacing the a-hydrogen in the clay by anhydrobasic groups. This cannot be so readily observed in the commercial manufacture of these cements, as silica, alumina, lime, alkali, etc. (in the form of impurities in the coal), are added to the materials in the original mixture and produce other types than those here described in detail.

To obtain some idea of the influence of the temperature and duration of the heating it is necessary to use the dynamisation theory (p. 108). According to this, the oxygen valencies which are in a saturated state in the raw material are set free when the clay, etc. is heated to its vitrification point. If the heating is prolonged or the temperature rises much above that needed to produce vitrification, polymerisation products are formed and the free oxygen valencies again become partially or completely bound. If the heating is still further prolonged or the temperature is raised until the material melts, an increase in the density of the basic silicates present may be observed. At the melting point of the material, the polymerisation attains a maximum; the maximum density must, of necessity, be reached simultaneously. This change in density under the influence of heat has been repeatedly observed by various investigators as well as by the authors of the present volume.

From these considerations it follows that the activity of the basic salts (which is due to the liberation of secondary oxygen valencies at the vitrification temperature of the material) is diminished or even destroyed on prolonged heating at a temperature approaching the melting point.[393]

Both consequences of the theory—(*a*) the increase in density on prolonged heating, attaining of a maximum at the melting point, and (*b*) the diminution of activity or ability to hydrate—are fully confirmed by the facts.

In confirmation of the second consequence of the theory, the following facts may be cited : A properly burned cement, if crushed to powder and then mixed with a suitable proportion of water, readily hydrates at the ordinary temperature. This property of cement diminishes on prolonged heating at the vitrification point and, in some cases, ceases entirely when the cement is fused.

If the temperature is raised much above the melting point, further reactions may occur, the polymerised molecule breaking up into its original constituents—i.e. into single cement molecules—or decomposition occurs within the cement molecule itself. In the former case, useful cements are produced. Schmidt and Unger have prepared crystalline Portland cements from such fused substances by means of the electric arc. Sauer has investigated the optical properties of these crystals. When crushed and mixed with water they set rapidly, with an appreciable development of heat.

This theory of the formation of polymerisation products of aluminosilicates (including calcium aluminosilicates) at high temperatures, provides a simple explanation of several facts which have hitherto proved puzzling. Among several others :

The Reactions which occur on granulating furnace slags and the formation of Silicate Cements from them[303b]

are thereby explained.

The raw materials from which iron is obtained are the iron ores. In addition to iron, these contain other earthy constituents such as lime, silica and alumina. The object of smelting these ores with coke in furnaces is to separate the metallic iron from the other materials and to remove the latter in a fluid state as slags. In order that the slags may possess the necessary fluidity, the lime must bear a certain ratio to the silica and the alumina, and great care is exercised by iron-smelters to ensure that this ratio is maintained. In most cases, the proportion of lime in the raw iron ores is too low and an addition of limestone is, therefore, made. Under favourable conditions, the molten iron and slag separate readily in the furnace on account of the great difference in their specific gravities, and are allowed to flow separately out of the furnace at two different levels. The slag carries off all the lime, silica and alumina in the form of a calcium aluminosilicate.

If the slag is " quenched," by allowing it to fall into cold water, a material is obtained which, if crushed to a fine powder and mixed with alkaline solutions (lime-water, etc.), hardens to a strong mass. The material which has not been granulated does not possess this property.

The simplest explanation for this difference in behaviour between

slags which have been granulated and others is that the latter are polymerised, whereas the quenched or granulated slags undergo an "entpolymerisation," i.e. a breaking up into single cement molecules.

Against this view it may be argued that these slags are only mixtures and not chemical compounds, but no satisfactory proof has been found in support of this objection. On the contrary, it is obvious that the manner in which these slags are produced is neither irregular nor capricious, but is in accordance with definite "laws," their composition only varying in the several works because of differences in the iron ores used.

Hence, if an iron ore of constant composition is used in a given works, the composition of the slags will also be constant. This consequence of the authors' new theory of the constitution of slags is adopted by Jantzen[304], who supports it by the following analyses of furnace slags from the Buderus Iron Works in 1888 to 1890, 1893, 1895 and 1899:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	$CaSO_4$	CaS	MgO	Alkalies
1888–90	35.20	10.02	0.21	0.55	0.30	47.19	1.56	2.17	1.20	(not determined)
1893	34.50	10.90	0.18	0.64	0.46	47.44	1.44	1.99	1.30	" "
1895	34.23	10.28	0.33	0.64	Trace	48.29	1.87	2.07	1.13	" "
1899	35.40	10.45	0.91		0.37	46.74	1.72	1.81	1.20	" "

This remarkable regularity in the composition of the slags during so long a period cannot be a mere coincidence. It is far more characteristic of a definite law, such as is only observed in connection with the formation of definite chemical compounds.

Allen and Shepherd[737] deny that this constancy of composition is due to the reason stated and regard it as caused by the constant composition of the mixture charged into the furnace. They endeavour to support their contention by stating that many minerals have been found in such slags, and protest against speculations on the structural chemical nature of substances of which the molecular weight is unknown. The obvious reply to such a criticism is that it is quite beside the point. There is no evidence in support of the view that the composition of the slags is dependent on that of the charge, except in so far as all chemical reactions require certain proportions of raw materials before they can occur. The fact that the charge is constant, or variable within certain limits, is not incompatible with the formation of definite chemical compounds.

The further allegation that such slags contain many minerals is not supported by facts. Jantzen, who arrived at the same conclusion as the authors of the H.P. theory, concerning the slags he examined, must have reached a widely different conclusion if the slags had really contained numerous minerals.

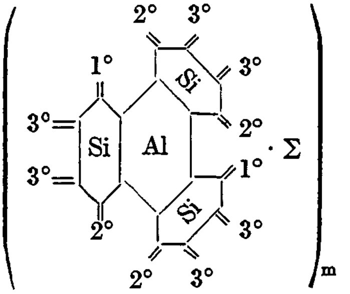
If Allen and Shepherd insist on regarding slags as a kind of "glass," i.e. as a mixture, it is difficult to see how they can explain satisfactorily the results of Lunge's experiments (pp. 160 and 171) on the behaviour of granulated and ungranulated slags with alkalies. It would be a most

remarkable coincidence if such slags behaved so completely in accordance with the H.P. theory, if this theory were quite erroneous.

With regard to the determination of the molecular weight of the constituents of slags, it is one of the advantages of the H.P. theory that (as has been previously pointed out) it furnishes for the first time a fully established hypothesis concerning the minimum molecular weight which a substance can possess when in the solid form. The determination of this minimum has been impossible hitherto, as no method yet known—not even the physico-chemical ones used for soluble compounds—is applicable to solids. The published molecular weights are, as the present writers have shown elsewhere, only applicable to substances in gaseous form or in solution, and cannot be used for substances in a solid state. The charge of lack of knowledge of molecular weight of the compounds concerned cannot, for this reason, be urged in opposition to the H.P. theory.

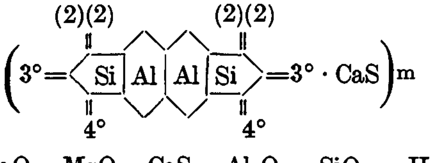
Previous theories as to the nature of furnace slags have led to most puzzling results. The theory that the chief constituent of these slags is a definite chemical compound is confirmed by the fact that analytical results obtained by Jantzen agree well with the formula :

$$26\,CaO \cdot 1.5\,MgO \cdot 0.25\,FeO \cdot 0.25\,MnO \cdot 3\,Al_2O_3 \cdot 18\,SiO_2 \cdot CaS \cdot 0.5\,CaSO_4$$



An experimental proof of the authors' views of the constitution of furnace slags is to be found in an investigation of slowly cooled and of granulated slags by Lunge[305], who obtained the following results :

$$21.5\,CaO \cdot 0.5\,MgO \cdot 2\,H_2O \cdot 6\,Al_2O_3 \cdot 10\,SiO_2 \cdot CaS$$



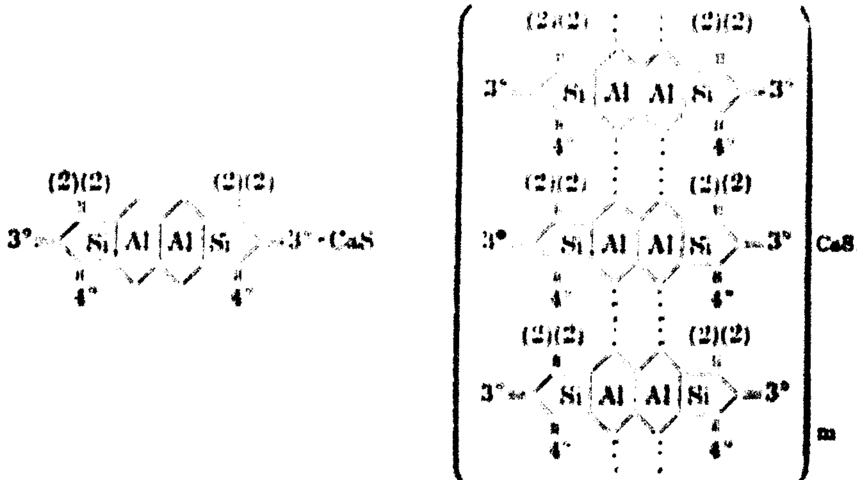
	CaO	MgO	CaS	Al_2O_3	SiO_2	H_2O	φ
Calculated	47.46	0.78	2.82	23.93	23.60	1.41	—
Found in...... (a)	47.17	0.73	1.82	24.36	23.38	1.06	0.72
Granulated slag (b)	47.14	0.73	1.82	24.20	23.60	1.25	0.84
Found in........ (a)	46.38	0.81	1.79	24.64	23.29	1.21	0.98
Ungranulated slag (b)	46.40	0.81	1.79	24.82	23.50	1.17	1.10

φ Unattacked by caustic soda or sodium carbonate.

The experiments from which these results were obtained are shown in the following Table :

Nature of Treatment	Dissolved out of granulated slags			Dissolved out of ungranulated slags		
	SiO_2 %	Al_2O_3 %	Mol. SiO_2 to 1 Mol. Al_2O_3	SiO_2 %	Al_2O_3 %	Mol. SiO_2 to 1 Mol. Al_2O_3
I. Heated for 2 hrs. with 30 per cent caustic soda solution	6.93			7.25	6.36	1.91
	6.93	5.94	1.9	7.25	6.34	1.91
II. Heated for 2 hrs. with 10 per cent caustic soda solution	1.09	2.57	0.72	1.76	0.15	—
	0.88	2.33	0.40	1.48	0.17	—
III. Digested for 6 hrs. on a water bath with 10 per cent caustic soda solution	2.30	3.43	1.15	2.68	0.13	—
	2.12	3.53	1.03	2.87	0.15	—
IV. Heated for 2 hrs. with 5 per cent caustic soda solution	1.92	2.63	1.25	2.43	0.12	—
	1.80	2.74	1.13	2.74	0.11	—
V. Digested for 6 hrs. on a water bath with 5 per cent caustic soda solution	3.53	4.12	1.47	4.25	0.31	—
	3.00	4.81	1.06	4.40	0.28	—
	3.52	4.91	1.23	4.48		—
" " " "	3.52	4.40	1.37	4.40		—
VI. Heated for 2 hrs. with 5 per cent sodium carbonate solution	1.26			4.68		—
	1.15			4.70	—	—
VII. Heated for 6 hrs. on a water bath with 5 per cent sodium carbonate solution	1.19			5.06	—	—
	1.14			5.08		—

It will be observed that a 30 per cent. solution of caustic soda attacks both kinds of slag so strongly as to resemble the effect of fusing them with soda. For this reason no importance should be attached to the fact that rather more is dissolved from the ungranulated slag than from the other. The relative behaviour of both slags towards 10 per cent. caustic soda solution should be noted, especially the fact that the granulated slag is the more soluble of the two. On comparing the structural formulæ of the two slags



Granulated Slag. Ungranulated Slag.

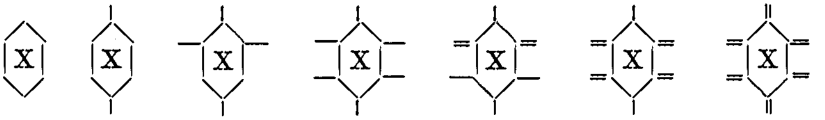
this difference is easily understood. Through the combination of a large number of cement molecules to form a combined molecule the strength of the bonds of the alumina in the ungranulated slags is greatly reduced.

On the other hand, it appears as if the combination of several silicate molecules, to form a single large one, weakens the bond in the pentites ; otherwise, no explanation can be given for ungranulated slags giving up 4 to 5 times as much silica to sodium carbonate solution as do granulated slags.

(c) A New Theory of Hardening

Various theories of hardening are stated briefly in the *Bibliography*.[305a] None of them are entirely satisfactory, hence the need for a fresh hypothesis based on the hexite-pentite theory.

In the following formulæ is shown the composition of various hydrated hexites, derived from one which is capable of taking up hydroxyl progressively, i.e. at different intervals of time :



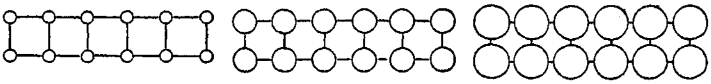
$6XO_2$, $H_2O{\cdot}6XO_2$, $2H_2O{\cdot}6XO_2$, $3H_2O{\cdot}6XO_2$, $4H_2O{\cdot}6XO_2$, $5H_2O{\cdot}6XO_2$, $6H_2O{\cdot}6XO_2$

a b c d e f g

The conversion of *a* into *b*, *b* into *c*, *c* into *d*, and so on, is accompanied by an increase in the volume of the molecules concerned, so that the molecular volume of *b* is greater than that of *a* ; that of *c* is greater than that of *b*, and the compound *g* has the largest molecular volume of the whole series.

In converting the compound *a* into *b*, *b* into *c*, and so on, the separate molecules in each group take up definite positions relative to each other, so that between *b*, *c*, *d*, *e*, etc., definite attractive, or more correctly molecular, forces are bound to exist.

Assuming the molecules to be in the form of minute spheres, the last statement may be expressed graphically by the following diagrams :



b Molecules c Molecules d Molecules

Each addition to the molecule of water in the form of hydroxyl groups,[305b] with a corresponding increase in the size of the molecule, is termed a *hydration phase*. It is clear that any substance which is submitted to a sufficient number of hydration phases must set and harden, because with the increase in the molecular volume the space between the various molecules must diminish and their mutual attraction or molecular force must correspondingly increase. Hence, every substance

which can take up water progressively, i.e. which can undergo a series of hydration phases, must be a hydraulite (see footnote p. 153).

Experience has shown that if the first hydration phases follow each other rapidly, either no hardening occurs or what little hardening takes place is very feeble.

These facts may be explained in accordance with the new theory, by stating that if the hydration phases follow each other rapidly, the spaces between the molecules are too large, or at any rate much larger than when the hydration occurs more slowly. If this explanation is correct, it should be possible to treat substances which hydrate rapidly and do not harden in such a manner (as by applying pressure) that the molecules are brought nearer together. The facts prove that when this is done, the substance sets and hardens, thus fully confirming the theory. Quicklime is a typical example of a material with rapid hydration phases, and when it is slaked it falls completely to powder with a considerable development of heat and the evolution of clouds of steam. According to Knapp[306], however, very finely ground quicklime when mixed with water in a suitable, tightly closed vessel produces, after several hours, a material which is harder than ordinary black-board chalk.

From the foregoing statements, the following conditions and characteristics of good hydraulites may be deduced :

1. The earlier hydration phases must occur at sufficiently long intervals.

2. The material must undergo a large number of hydration phases. Of several substances, under similar conditions, the one which undergoes the most hydration phases will eventually be the hardest and the most dense.

3. The smaller the distance between the molecules of a hydraulite during the first hydration phases, the harder and denser will be the mass produced.

The New Theory of Hardening and the Facts

I. According to this theory, setting must be prevented if the particles of hydraulite are too far apart, as when too much water is used.[307] An excess of water may also bring about too rapid an addition of OH-groups and this, according to the new theory, must have a detrimental effect.

II. It also follows from the theory that the smallness of the hydraulite particles must play a special part in setting and hardening. The smaller the particles the easier and more rapid will be the hydration ; the larger the particles the more difficult will it be to hydrate them. A definite degree of fineness is, therefore, an essential condition of hydration, and it is theoretically, as well as practically, necessary to regulate the intervals of time between the hydration phases (i.e. the rate of combination with water) by means of the fineness of the particles of cement.

III. According to Knapp[308], anhydrous magnesia (prepared by calcining magnesium chloride) absorbs water with no development of heat and with extreme slowness, a stony mass is produced with a hardness somewhat greater than that of marble. The lighter, more porous magnesia (obtained from the hydrous carbonate) combines rapidly with water and finally forms a porous, talc-like mass.

Richter[309] maintained finely powdered, anhydrous calcium nitrate at a white heat for six hours in a platinum crucible and obtained a vitrified porcelain-like mass, with a clearly defined crystalline texture on the fractured surface. When ground with water this crystalline CaO sets like cement. If the lime is insufficiently heated it is found to crack badly on cooling.

Allen and Shepherd[737] state that only large pieces of fused lime are indifferent to water, and that finely powdered, fused lime does not differ from ordinary quicklime. This "fact," which requires confirmation as it contradicts the results of Richter's investigations, is used by Allen and Shepherd as evidence against the H.P. theory. These critics consider that the reduced reacting power of the burned material is not due to polymerisation, but to the size of the pieces, i.e. to the surface area. If this were really the case, calcium aluminosilicates (cements) must behave exactly the same when burned hard or soft, provided that the material is ground to the same degree of fineness in both cases. Direct experiments show, however, that this is not the case.

These interesting instances of isomeric lime and magnesia are readily understood in the light of the authors' theory ; both the MgO from magnesium chloride and the crystalline CaO are polymerisation products which have hydration phases like the hydraulites and harden in a similar manner.

According to the authors' theory, the cause of disintegration in some materials is due to hydration phases following each other too rapidly, owing to the material not having been properly burned. In this connection it must be admitted that disintegration may also be due to other causes.

For instance, Michaelis[310] attributes the cracking or "expansion" of cements to a subsequent increase in volume, this being due to three causes : first and foremost to a high percentage of lime, second to the presence of calcium sulphate, and, finally, to irregular particles and coarse grains in the cement.

That too high a percentage of lime may bring about the destruction of the mass is a simple inference from the authors' theory, as lime and alkalies effect an intense and rapid hydration, and a sufficiently large proportion of lime will cause the hydration phases to follow each other very rapidly.

An irregular distribution of coarse and fine grains in the cement, resulting in disintegration, may be explained in terms of the authors' theory because, as already mentioned, a fine powder is hydrated more

rapidly than a coarser one and forces differing in intensity are thereby set to work in various portions of the material, with the result that the latter is broken up.

The harmful effect of gypsum or plaster of Paris in silicate cements is described later.

IV. Quartz crushed to an impalpable powder and then levigated, will not form a hard mass with lime and water.[311] Opal, similarly treated, hardens slowly, but well. Calcined silica, such as that obtained in silicate analyses, when mixed with lime, hardens rapidly but badly.

According to the authors' theory, lime effects a hydration of the opal and calcined silica, so that they harden; but, as lime does not behave in this way towards quartz, with the last-named substance no hardening occurs.

According to Winkler[312], if a mixture of three parts of quartz and one part of lime is strongly heated and the sintered mass is then crushed with six times its weight of lime and a suitable quantity of water, the mass hardens slowly and strongly. It is clear that in this case a series of hydration phases occurs at long intervals.

V. The authors' dynamisation theory also explains why it is necessary for most silicates to be heated to redness before they will harden in water (like Portland cements), or with lime and water (like puzzolans). In the case of clays it has already been shown that, on heating them to redness, or on causing them to combine with a base, the bond between the hexites or pentites of silicon and aluminium is weakened, and, for this reason, such silicates precipitate gelatinous silica when treated with dilute acids.

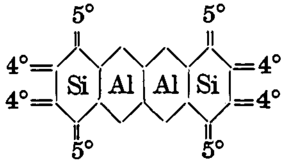
The authors' theory agrees with the discovery of Fuchs that only those silicates harden which contain "soluble silica," with the one difference that the "soluble silica" plays absolutely no part in the hardening process.

Different silicates must be heated[314] to very different temperatures or for various periods before they will harden with lime and water. For some of them a short heating to redness is sufficient; others must be strongly heated for a considerable time, and others must be almost melted. According to Fuchs, the following substances harden with lime and water after they have been sufficiently heated at a suitable temperature: felspars, leucite, various magnesium silicates such as talc and steatite, analcime, natrolite, clays, etc. All these silicates harden because the heating and subsequent treatment with lime and water produce hydration phases in the manner already explained.

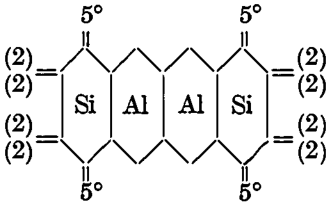
The cause of the hardening of "trass" and "puzzolans" with lime and water may be explained in an analogous manner. The trasses and puzzolans are simply clays, and only differ from ordinary clays in the alterations they have undergone in consequence of volcanic action. In the course of time these substances may again lose their free secondary valencies. Such trasses or puzzolans are improved by being heated to redness.

A considerable number of hydraulites of the most widely different composition have already been prepared. Thus, various aluminates, ferrites, ferromanganese oxides and silicates, borates, calcium sulphates, etc., have marked hydraulic properties. A further study of the hardening of these compounds must eventually lead to the proof of the existence of hydration phases.

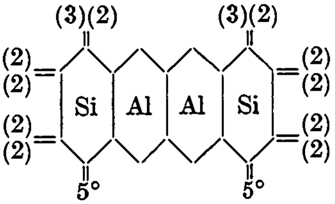
VI. *The Causes of Hardening of Portland Cements.* If a definite silicate cement is selected, e.g. the compound



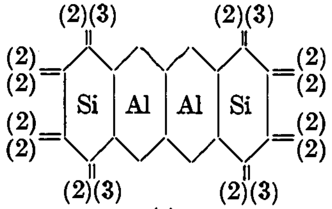
the following substances may be formed from it :



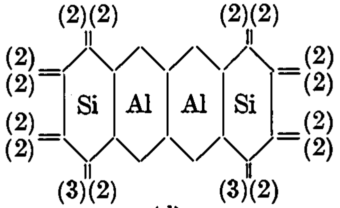
(a)



(b)

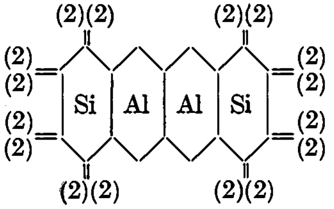


(c)



$+ 2\,Ca(OH)_2$

(d)



$+4\,Ca(OH)_2$ etc. etc.

If the hydration occurs as indicated in the above formulæ at definite intervals and with a definite increase in volume, hydraulites are produced in accordance with the authors' theory. The absorption of water does actually occur in this manner, as will be explained in the next chapter ; Zulkowski[315] has experimentally proved the increase in volume. He treated ground slag with water, and obtained a flocculent

mass and a deposit of a sandy nature. The volume of the deposit increased in process of time. The microscopical appearance of this ground slag after treatment with water differed but little from that of the dry (untreated) material.

The action of alkaline fluids was much more energetic. The volume of the deposit was three to five times that of the original slag-powder. Under the microscope the appearance of the material gradually changes, and after several months the original, small, glassy grains were no longer observable, their place being taken by much larger, irregular rounded grains or masses.

In the case of Portland cement, water alone will effect a change in shape similar to that which occurs with slag-meal and alkaline solutions. Zulkowski was the first to point out these changes in shape and volume in the case of silicate cements, and in these changes he saw the true cause of the hardening of hydraulic materials. The hardening itself he explains as follows: "The cement grains which, at the commencement, lie over and amongst each other and without any definite relationship to each other, combine chemically with the water present in the pores; from them is produced a new substance, a hydrosilicate, the material thereby changing its shape and increasing in volume. The particles which expand in this manner occupy all the available space, lie closely together, increase continually in volume, and eventually convert the whole of the original loose particles into a compact mass."

[W. Michaelis (*Chem. Zeit.*, 1893, 17, 982) has suggested that hardening is mainly due to the formation of a colloidal calcium hydrosilicate. According to Desch[19], "this theory so well explains the phenomena observed and is in such good accordance with the results of microscopical investigation of cements during and after setting that it must be held to contain the greater part of the truth." Desch further adds that "the course of events when Portland cement is mixed with water may be described as follows: The essential hydraulic constituent is *alite*, which is a solid solution of three components. The action of the water is, at first, confined to the *alite*, which is partly decomposed, the aluminates being first hydrolysed. The solution thus produced is supersaturated and soon deposits tricalcium aluminate partly in colloidal form and partly in crystals, according to the amount of water in the mixture, a larger proportion of water favouring crystals and a smaller one the formation of a gel. The excess of lime remains in solution or a part may be deposited as crystals of calcium hydroxide. This corresponds to the 'initial set.'

"The action of the water on the calcium silicate contained in the *alite* is much slower, and when hydrolysis occurs the calcium silicate is separated in colloidal form. The gel produced forms a coating round the particles and prevents further action. The colloidal matter is easily seen in a polished and etched specimen, and its definitely colloidal nature may be shown by immersion in a dye such as eosin. Colloidal substances adsorb dyes, but crystals do not do so."

Desch attributes the hardening of cement which has been hardened and re-ground to the large proportion of non-hydrated matter present in all cements, owing to the slowness of the hydration.

The suggestion of W. Michaelis that the hardening of cements is due to their colloidal nature cannot *per se* be regarded as of more than limited value, even when supported by the statement of C. Desch that it "is in such good accordance with the results of microscopical investigation." It does not coincide with the results of Feichtinger's studies of hydration, given on another page, nor with the thermal investigations of Oswald and the multitude of facts which have been published in support of various other theories, and is therefore inapplicable to any general theory relative to cements. There is an analogy between the action of water on cements and on colloids, as has been pointed out on a previous page, and any theory (if

correct) must therefore be capable of extension to organic cements in which hydrosols are converted into hydrogels, forming cementitious substances, just as inorganic cements pass through definite hydration phases into stone-like masses.

Bone-substance, which is essentially a highly basic calcium carbo-phosphate (p. 271), is probably derived from an organic cement whose hardening phases are analogous to those of Portland cement.]

The Consequences of the New Theory of Portland Cement and the Facts

From the foregoing theory of the chemical constitution of the Portland cements and the corresponding hardening theory, a series of interesting consequences may be inferred, the value of which may be proved by means of the experimental material available.

A

From the theory it follows that the calculation of the formulæ of Portland cements from their analyses must lead to compounds, the existence of which is theoretically possible. The calculation of the formulæ from a series of cement analyses fully confirms this consequence of the theory ; the high content of bases is particularly noticeable in some analyses. Whether the whole of the base is in actual combination is doubtful ; further investigations are needed to decide it.

The formulæ calculated from cement analyses (see *Appendix*) are shown in the following Tables :

(a) $n\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$.

	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
I. $24\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	1.50	1.50	26.00	1.00	0.25	0.25	0.5	3	2
II. $34\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2$	2.00	1.00	34.00	—	—	—	—	—	—
III. $35\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2$	2.00	1.00	35.00	—	—	—	—	—	—
IV. $36\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.00	1.00	36.00	0.50	—	—	0.5	—	—
V. $37\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.00	1.00	36.00	1.50	—	—	0.5	—	—
VI. $37\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.00	1.00	36.25	1.25	—	—	0.5	—	—
VII. $37\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.25	0.75	36.00	2.00	—	—	1.0	—	—
VIII. $38\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.25	0.75	38.00	0.50	—	—	0.5	—	—
IX. $39\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.00	1.00	38.25	1.25	—	—	0.5	—	—
X. $39\,MO \cdot 3\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	2.50	0.50	39.00	1.00	—	—	1.0	—	—

(b) $n\,MO \cdot 3\,R_2O_3 \cdot 10\,SiO_2$.

	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XI. $29\,MO \cdot 3\,R_2O_3 \cdot 10\,SiO_2$	3.00	—	29.0	—	—	—	—	—	—
XII. $34\,MO \cdot 3\,R_2O_3 \cdot 10\,SiO_2$	2.25	0.75	31.5	2.5	—	—	—	—	2
XIII. $35\,MO \cdot 3\,R_2O_3 \cdot 10\,SiO_2$	2.25	0.75	32.5	1.5	0.5	0.5	—	—	—

(c) $n\,MO \cdot 3\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$.

	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XIV. $52\,MO \cdot 3\,R_2O_3 \cdot 18\,SiO_2$	—	3.00	52.00	—	—	—	—	—	—
XV. $54\,MO \cdot 3\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	2.25	0.75	53.75	1.25	—	—	1	—	—

(d) $n\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$.

		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XVI.	$20\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.00	1.00	22.0	1.0	0.25	0.25	0.50	3.0	1
XVII.	$21\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.00	1.00	22.0	0.5			0.50	1.0	2
XVIII.	$21\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.00	1.00	22.5	1.0	0.25	0.25	0.50	2.5	1
XIX.	$22\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.00	1.00	22.0	0.5	0.25	0.25	0.50	0.5	2
XX.	$24\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	1.50	1.50	26.5	1.5		0.25	0.75	4.0	2
XXI.	$25\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	1.50	1.50	27.0	1.5	0.25	0.25		4.0	2
XXII.	$30\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.50	0.50	30.0	2.5	0.50	0.50	1.00	0.5 MnO	—
XXIII.	$42\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.00	1.00	42.5	1.5	0.50	0.50	0.50	2.5	2
XXIV.	$45\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.50	0.50	45.0	1.0			1.00		—
XXV.	$45\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.25	0.75	44.0	1.0	0.25	0.75	1.00	—	—
XXVI.	$48\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.25	0.75	45.5	1.0	—		0.50	—	—
XXVII.	$48\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$	2.25	0.75	46.0	1.0	—		1.00	—	—

(e) $n\,MO \cdot 6\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$.

		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XXVIII.	$92\,MO \cdot 6\,R_2O_3 \cdot 12\,SiO_2 \cdot \Sigma$	5	1	89	3	—		—	3	10

(f) $n\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$.

		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XXIX.	$38\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	3.5	2.5	40.0			0.5	0.5	2	2
XXX.	$39\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	3.5	2.5	40.5	0.5		0.5	0.5	2	3
XXXI.	$74\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	5.0	1.0	71.0	6.0		—	—	3	8
XXXII.	$76\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	5.0	1.0	72.0	5.0		—	—	1	4
XXXIII.	$90\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	5.0	1.0	86.0	8.0		—	—	4	10

(g) $n\,MO \cdot 6\,R_2O_3 \cdot 16\,SiO_2 \cdot \Sigma$.

		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O	FeO	MnO
XXXIV.	$36\,MO \cdot 6\,R_2O_3 \cdot 16\,SiO_2 \cdot \Sigma$	6		35.50	3.50		—	1.0	2.00	30	—	—
XXXV.	$38\,MO \cdot 6\,R_2O_3 \cdot 16\,SiO_2 \cdot \Sigma$	6		35.75	3.25	0.50	0.50	1.5	1.50	26	0.5	0.5
XXXVI.	$39\,MO \cdot 6\,R_2O_3 \cdot 16\,SiO_2 \cdot \Sigma$	6		34.00	3.00	1.00	1.00	1.0	—	—	0.5	0.5
XXXVII.	$39\,MO \cdot 6\,R_2O_3 \cdot 16\,SiO_2 \cdot \Sigma$	6		35.75	3.25	0.50	1.00	1.5	1.00	30	0.5	0.5
XXXVIII.	$40\,MO \cdot 6\,R_2O_3 \cdot 16\,SiO_2 \cdot \Sigma$	6		34.75	3.25	0.75	1.00	0.5	0.25	—	0.5	0.5

(h) $n\,MO \cdot 5\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$.

		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XXXIX.	$44\,MO \cdot 5\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	3.5	1.5	44.5	1.0	0.5	1.5	0.5	3	2.5
XL.	$50\,MO \cdot 5\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$	4.0	1.0	50.0	1.0	—	—	1.0	—	—

(i) $n\,MO \cdot R_2O_3 \cdot 12\,SiO_2$.

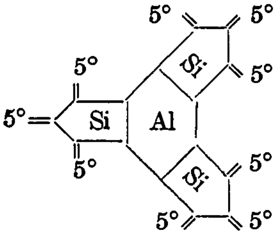
		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CO_2	H_2O
XLI.	$30\,MO \cdot R_2O_3 \cdot 12\,SiO_2$	0.75	0.25	29.5	0.5	—	—	—	—	—
XLII.	$32\,MO \cdot R_2O_3 \cdot 12\,SiO_2$	0.75	0.25	32.0	—	—	—	—	—	—
XLIII.	$34\,MO \cdot R_2O_3 \cdot 12\,SiO_2$	1.00	—	33.5	0.5	—	—	—	—	—
XLIV.	$39\,MO \cdot R_2O_3 \cdot 12\,SiO_2$	1.00	—	39.0	—	—	—	—	—	—

The water which enters into combination must, in any case, be capable of representation by stoichiometrical figures, i.e. in molecules. That this can be done is seen from the following examples :

I. Von Teicheck[316] has studied the hydration of a Portland cement of the formula

$$45\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot R'_2SO_4 \begin{cases} 45\,MO = 44\,CaO \cdot 1\,MgO, \\ 3\,R_2O_3 = 2.25\,Al_2O_3 \cdot 0.75\,Fe_2O_3, \\ R'_2O = 0{,}75\,Na_2O \cdot 0.25\,K_2O \end{cases}$$

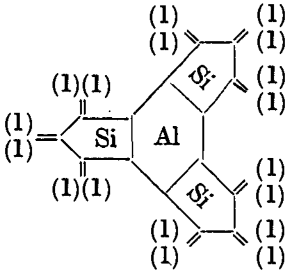
(see *Appendix*, Analysis XXV).



After 21 or 30 days 14·44 per cent. of hydration-water was found, which, according to theory, represents the addition of 36 mols. of water, as shown in the following equation :

$$45\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot R'_2SO_4 + 36\,H_2O$$
$$= 18\,MO \cdot 9\,H_2O \cdot 3\,R_2O_3 \cdot 15\,SiO_2 + 27\,M(OH)_2 + R'_2SO_4$$

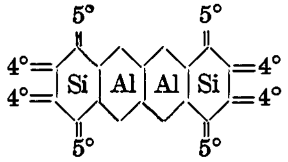
In this case, the chief products of the reaction may be represented by :



$+ 27\,M(OH)_2 + R'_2SO_4$

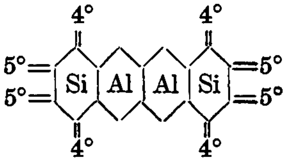
The percentage of water represented by the above formula is 14·21, which is in sufficiently close agreement with that found by experiment.

II. Zulkowski[317] produced a cement by burning, at a white heat in a Seger furnace, a mixture of lime and Zettlitzer kaolin, the latter having a composition corresponding to $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. His results suggest one of the two following formulæ for the cement he prepared :



$36\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

or



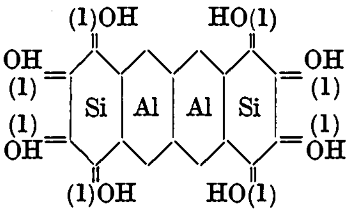
$36\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

Zulkowski studied the hydration of this compound by reducing it to a powder, mixing it with water and forming balls; these set when warmed gently for a quarter of an hour and became quite hard after one and half hours. These balls were then placed in water and were found to have become much harder after the lapse of several months.

Zulkowski also found that a given cement after 7 days contained 16·19% and after 30 days 17·05% of hydration-water. According to theory, 36 mols. of water should enter into combination according to the following equation :

$$36\,CaO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 + 36\,H_2O$$

=

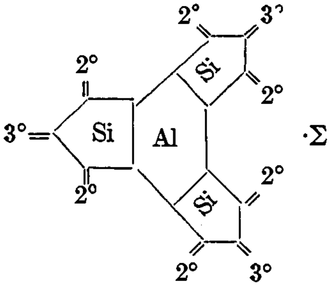


$+ 28\,Ca(OH)_2$*

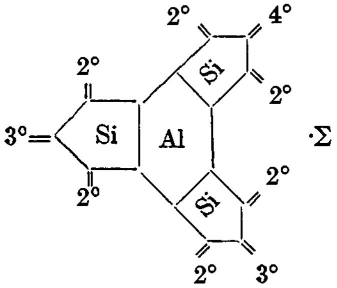
The value 16·19% calculated from this formula agrees sufficiently well with the amount found by experiment.

C

The hydration of cements must take place very gradually. In determining the amount of water entering into combination during the hardening it is, therefore, necessary to be able to trace a gradual increase in the proportion of water in the material. This is confirmed by the results of a series of hydration experiments by Feichtinger[319], who studied the behaviour, towards water, of the following hydraulic materials :



$21\,MO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$†
(Analysis XVIII, *Appendix*)
1 (B)

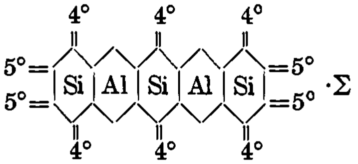


$22\,CaO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma$‡
(Analysis XIX, *Appendix*)
2 (C)

* 4000.8 gms. of the hardened cement mass contain $18 \times 36 = 648$ gms. water or $\frac{64800}{4000.8} = 16.19$ per cent. water.

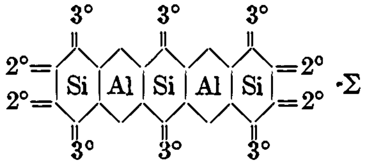
† $\Sigma = 2.5\,R''CO_3 + 0.5\,R_2SO_4 + H_2O$.

‡ $\Sigma = 0.5\,MgCO_3 + 0.5\,R_2SO_4 + 2\,H_2O$.



$44\,CaO \cdot 5\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$*
(Analysis XXXIX, *Appendix*)

3 (A)



$26\,CaO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot \Sigma$†
(Analysis XXX, *Appendix*)

4 (D)

Samples B, C and D were Bavarian hydraulic limes, obtained by burning marl; A was a Portland cement. The sample D contained 13 mols. free lime (as shown by Feichtinger's experiments), but in the other silicates the whole of the lime was in a combined state.

The hydration experiments were carried out as follows: a small quantity of cement was placed in a suitable vessel and weighed accurately. It was then mixed with a little water and was afterwards immersed in water. To determine the amount of water which had entered into combination, the samples were dried at 100° C. and the increase in weight was attributed to the combined water.

Calcium hydrate only loses all its water at a red heat; at 300° C. only a portion of it is removed. According to Feichtinger, the silicate-water is also driven off at this temperature. By determining the proportion of water evolved at 300° C. and deducting it from the total combined water, the difference shows the proportion of water in combination with the lime.

The following Tables—which are based on Feichtinger's researches—show the manner in which the water was evolved.

In Table I:

g=the total weight of water which combines with 100 parts of cement in time t.

s=the weight of water which is evolved at a red heat from 100 parts of the mixture of cement and water at 300° C, i.e. water combined with the silicate.

$g-s$=the weight of water which is evolved at red heat from 100 parts of the mixture of cement and water, i.e. water combined with lime as $Ca(OH)_2$.

* $\Sigma = 1.5\,R''CO_3 + 1.5\,R_2CO_3 + 0.5\,R_2SO_4 + 2.5\,H_2O$.
† $\Sigma = 2\,R''CO_3 + 0.5\,Na_2SO_4 + 13\,CaO + 2\,H_2O$.

Table I

	1 (B)			2 (C)			3 (A)			(4) D		
t	g	s	$g-s$	g	s	$g-s$	g	s	$g-s$	g	s	$g-s$
Immediately after mixing with water.	1.28	1.28	—	0.61	0.61	—	0.99	0.99	—	6.79	1.40	5.39
After 4 hrs.	1.67	1.67	—	0.71	0.71	—	1.41	1.41	—	7.80	2.42	5.38
" 20 "	2.08	2.08	—	1.14	1.14	—	2.29	1.60	0.69	8.26	3.08	5.18
" 3 days	3.42	3.42	—	1.82	1.82	—	5.62	3.80	1.82	8.87	3.30	5.57
" 7 "	3.85	3.85	—	2.15	2.15	—	6.58	4.76	1.82	11.20	4.20	7.00
" 14 "	4.46	4.46	—	2.63	2.63	—	7.96	5.90	2.06	11.80	4.64	7.16
" 18 "	5.00	4.40	0.60	2.84	2.84	—	8.45	6.20	2.25	11.86	4.60	7.26
" 21 "	5.84	4.50	1.34	3.46	3.46	—	8.91	6.43	2.48	12.75	5.30	7.45
" 24 "	5.89	4.42	1.47	4.36	4.36	—	10.40	6.60	3.80	13.68	5.60	8.08
" 28 "	6.86	4.46	2.40	4.90	4.30	0.60	10.52	6.50	4.02	13.92	5.82	8.10
" 35 "	7.68	4.52	3.16	5.56	4.25	1.31	11.43	6.63	4.80	14.30	6.18	8.12
" 42 "	8.30	4.48	3.82	6.20	4.30	1.90	11.35	6.60	4.75	14.68	6.60	8.08
" 49 "	8.92	4.40	4.52	7.08	4.20	2.88	11.50	6.58	4.92	14.50	6.56	7.94
" 56 "	9.13	4.46	4.67	7.34	4.25	3.09	11.60	6.64	4.96	14.73	6.60	8.13
" 80 "	9.50	4.40	5.10	7.40	4.20	3.20	11.56	6.60	4.96	14.65	6.56	8.09

In Table II :

μ, μ_1, μ_2 and μ_3 are the molecular weights of the hydraulic binding materials.

γ=the number of molecules of water which combine with μ, μ_1, etc., parts of cement in time t.

σ=the amount of water, in gramme-molecules, lost by μ, μ_1, etc., parts of the mixture of cement and water at 300°, i.e. water combined with the silicate.

$\gamma-\sigma$=the number of molecules of water which are only evolved at a red heat from μ, μ_1, etc., parts of the mixture of cement and water, i.e. water combined with lime as $Ca(OH)_2$.

Table II

	μ=2777.4			μ_1=2659.4			μ_2=4585			μ_3=4327		
	1 (B)			2 (C)			3 (A)			4 (D)		
t	γ	σ	$\gamma-\sigma$	γ	σ	$\gamma-\sigma$	γ	σ	$\gamma-\sigma$	γ	σ	$\gamma-\sigma$
Immediately after mixing with water.	1.97	1.97	—	0.90	0.90	—	2.50	2.50	—	16.30	3.36	12.94
After 4 hrs.	2.58	2.58	—	1.04	1.04	—	3.59	3.59	—	18.75	5.82	12.93
" 20 "	3.21	3.21	—	1.68	1.68	—	5.97	4.07	1.90	19.86	7.40	12.46
" 3 days	5.27	5.27	—	2.69	2.69	—	14.32	9.68	4.64	21.33	7.93	13.40
" 7 "	5.94	5.94	—	3.17	3.17	—	16.77	12.13	4.64	26.93	10.19	16.74
" 14 "	6.88	6.88	—	3.97	3.97	—	20.28	15.04	5.24	28.37	11.16	17.21
" 18 "	7.73	6.79	0.94	4.19	4.19	—	21.53	15.80	5.73	28.51	11.06	17.45
" 21 "	9.01	6.94	2.07	5.11	5.11	—	22.70	16.38	6.32	30.65	12.74	17.91
" 24 "	9.08	6.82	2.26	6.44	6.44	—	26.50	16.82	9.68	32.89	13.46	19.43
" 28 "	10.58	6.88	3.70	7.24	6.35	0.89	26.80	16.95	9.85	33.46	13.99	19.47
" 35 "	11.85	6.97	4.88	8.21	6.28	1.93	29.13	16.89	12.24	34.38	14.85	19.53
" 42 "	12.81	6.91	5.90	9.16	6.35	2.81	28.92	16.82	12.10	35.29	15.87	19.42
" 49 "	13.76	6.79	6.97	10.46	6.20	4.26	29.30	16.77	12.53	34.83	15.77	19.08
" 56 "	14.09	6.88	7.21	10.85	6.28	4.57	29.56	16.92	12.64	35.41	15.87	19.54
" 80 "	14.66	6.79	7.87	10.93	6.20	4.73	29.45	16.82	12.63	35.22	15.77	19.45

These Tables agree with the theory in showing a gradual absorption of water. Thus 1 B, Table II, shows that on mixing the cement and water together only 2 mols. H_2O enter into combination, but that after 20 hours 3 mols., and after 18 days 7 mols. of water are combined. A gradual combination of water may also be observed in the case of silicates 2(C), 3(A) and 4(D).

It should be noticed that, according to Table II, some of the CaO in the materials studied by Feichtinger split off before the silicates had taken up the maximum quantity of water. Thus 1(B) can bind a maximum of 9 mols. of water, but the lime splits off when only 7 mols. (after 18 days) are combined. After 80 days this silicate took up no further quantity of water. A similar result is observable with 2(C), which is analogously constituted. In this case, the lime separates when 6 mols. have entered into combination, but only after 28 days. With Portland cement 3(A) the lime separates after the combination of 4 mols. of water, i.e. after 20 hours. In the compound 4(D) the hydration of the silicate molecule occurs somewhat rapidly, on account of the presence of free lime. After 20 hours the silicate molecule combined with about 7·5 mols. H_2O. The separation of the lime began only after 3 days, after 8 mols. of water had entered into combination.

The structural formulæ 1(B), 2(C), 3(A) and 4(D) show clearly the reason for the separation of the lime at an earlier stage than is the case with other hydraulites. The larger the basic side-chains the weaker must be the bond of a portion of the lime. The structural formula of Portland cement shows 4°- and 5°- side-chains, whereas the structural formulæ of the other compounds show at most only 2°- or 3°- side-chains.

The figures 16.82 and 15.77 molecules of σ-water,* which are taken up, after 80 days, from the compounds 3(A) and 4(D), at first appear to be opposed to the authors' theory, as for the latter the maximum is 10 mols. σ-water (or 11 or 12 mols. if the Al-OH-groups are included). From Feichtinger's results it is, however, clear that part of the water he regarded as σ-water was really in the form of "water of crystallisation." Feichtinger re-heated the cement masses 1(B), 2(C), 3(A) and 4(D) to redness and obtained a fresh hydration. These results are shown in Tables III and IV. From Table IV it will be seen that the cements 3(A) and 4(D) give similar results for σ. But, shortly after mixing, the cement 3(A) took up 7.49, and cement 4(D) 3.6 mols. of water, so that this portion of the water behaves differently from the remainder. If these amounts are regarded as "water of crystallisation," the remainder ($16.82 - 7.49 = 9.33$, and $15.77 - 3.6 = 12.17$) may be termed "water of constitution," i.e. the compound 3(A) has taken 9, and 4(D) about 12 mols. of silicate-water into combination in the form of hydroxyl groups.

* For definition of σ-water see previous page.

D

In silicate cements, such as Portland cement, which are devoid of free lime there can only be one, or at most two forms of water present at the beginning of hydration, viz. silicate-water and "water of crystallisation." After a short time a third form of water—that in the calcium hydroxide $Ca(OH)_2$—may be present. If, on the contrary, the cements contain free lime, the calcium hydroxide water is present at first in addition to the silicate-water and the "water of crystallisation" just mentioned.

These theoretical deductions are confirmed by Feichtinger's results previously mentioned. A glance at Tables I and II will show that Feichtinger found no calcium hydroxide water in cements 1(B), 2(C) and 3(A) (which contain chemically combined lime), but in cement 4(D), on the contrary, he found it shortly after the commencement of the hydration.[319a]

E

From the hardened masses it must be possible, by burning under certain conditions, to reproduce the original hydraulite with exactly the same hydrating (hardening) properties, so long as water is the sole hardening agent, as was the case in Feichtinger's experiments.

Several investigators, and particularly Michaelis[320], have drawn special attention to the possibility of reproducing the original cement powder from the hardened mass. This possibility of regenerating cements is, however, a simple deduction from the results[321] obtained by Feichtinger, who endeavoured to ascertain experimentally whether a hardened cement mortar when heated to redness and again mixed with water will re-set and harden. He also measured the amount of water taken up. His results are shown in the following Tables, in which the letters are the same as those in Tables I and II.

TABLE III

	1 (B)			2 (C)			3 (A)			4 (D)		
t	*g*	*s*	*g* − *s*	*g*	*s*	*g* − *s*	*g*	*s*	*g* − *s*	*g*	*s*	*g* − *s*
Immediately after mixing with water.	4.00	1.20	2.80	1.24	0.50	0.74	7.84	2.94	4.90	8.30	1.50	6.80
After 5 hrs.	4.20	1.60	2.60	2.30	0.70	1.60	7.89	3.02	4.87	—	—	—
„ 36 „	5.16	1.96	3.20	3.12	1.20	1.92	8.60	3.68	4.92	9.56	2.35	7.21
„ 60 „	5.48	2.02	3.46	3.80	1.40	2.40	9.20	4.35	4.85	—	—	—
„ 5 days	6.24	2.30	3.94	4.25	2.20	2.05	9.80	4.87	4.93	10.98	3.88	7.10
„ 8 „	6.56	2.58	3.98	4.40	2.32	2.08	10.50	5.60	4.90	—	—	—
„ 12 „	6.90	3.15	3.75	4.60	2.40	2.20	11.04	6.20	4.84	12.81	4.66	8.15
„ 20 „	7.75	3.84	3.91	5.48	3.35	2.13	11.84	6.56	5.28	14.60	6.52	8.08
„ 24 „	7.80	3.84	3.96	6.48	4.02	2.46	11.60	6.66	4.94	—	—	—
„ 40 „	8.32	4.11	4.21	7.06	4.22	2.84	—	—	—	—	—	—
„ 60 „	9.02	4.42	4.60	7.20	4.18	3.02	—	—	—	—	—	—

TABLE IV

	$\mu=2777.4$			$\mu_1=2659.4$			$\mu_2=4585$			$\mu_3=4327$		
	1 (B)			2 (C)			3 (A)			4 (D)		
t	γ	σ	$\gamma-\sigma$	γ	σ	$\gamma-\sigma$	γ	σ	$\gamma-\sigma$	γ	σ	$\gamma-\sigma$
Directly after mixing with water.	6.17	1.85	4.32	1.83	0.73	1.10	19.97	7.49	12.48	19.96	3.60	16.36
After 5 hrs.	6.48	2.47	4.01	3.39	1.03	2.36	20.10	7.69	12.41	—	—	—
„ 36 „	7.96	3.02	4.94	4.61	1.77	2.84	21.91	9.38	12.53	22.98	5.65	17.33
„ 60 „	8.46	3.11	5.35	5.61	2.06	3.54	23.44	11.08	12.36	—	—	—
„ 5 days	9.63	3.54	6.09	6.28	3.25	3.03	24.97	12.40	12.57	26.39	9.39	17.06
„ 8 „	10.12	3.98	6.14	6.50	3.43	3.07	26.75	14.27	12.48	—	—	—
„ 12 „	10.65	4.86	5.79	6.79	3.54	3.25	28.13	15.80	12.33	30.79	11.20	19.59
„ 20 „	11.96	5.92	6.03	8.09	4.95	3.14	30.17	16.71	13.46	—	—	—
„ 24 „	12.03	5.93	6.11	9.57	5.94	3.63	29.56	16.97	12.59	—	—	—
„ 40 „	12.84	6.34	6.50	10.43	6.23	4.20	—	—	—	—	—	—
„ 60 „	13.92	6.82	7.10	10.64	6.17	4.47	—	—	—	—	—	—

A comparison of the figures in Tables III and IV shows that the hydration phases of the regenerated hydraulite (made from a hardened cement by re-heating) follow each other more rapidly than do those of the original cement. From this it may be concluded that the hardened masses were not properly burned, as otherwise the hydration phases in the regenerated cement would occur in precisely the same manner as in the original cement. These results make the possibility of reproducing fresh cement from hardened masses highly probable.

As the hydration phases follow each other more rapidly than in the original cement (Tables I and II) a much lower degree of hardness must be obtained in the case of regenerated cements when they are mixed with water and allowed to set and harden. This was actually the case in Feichtinger's experiments.

F

Thermo-chemical studies of hydration and hardening processes must lead, in the case of cements which contain free lime, to results which are different from those in which the whole of the lime is in a combined state.

In cements of the former kind there are theoretical reasons why a development of heat must occur at the commencement of hydration (the hydration heat of the CaO); and in cements devoid of free lime a perceptible development of heat can only occur after an interval, viz. at the moment when the separation and hydration of the first CaO molecule occurs.

As a matter of fact, Feichtinger did observe a noticeable development of heat during the hydration of cement 4(D), which contains free lime.

In this connection the results of W. Ostwald's thermo-chemical studies [322] on the following cements are particularly interesting:

Analysis XII.*

A. $34\,MO \cdot 3\,R_2O_3 \cdot 10\,SiO_2 \cdot 2\,H_2O \begin{cases} 34\,MO = 31.5\,CaO \cdot 2.5\,MgO \\ 3\,R_2O_3 = 2.25\,Al_2O_3 \cdot 0.75\,Fe_2O_3. \end{cases}$

Analysis XXVIII.

B. $92\,MO \cdot 6\,R_2O_3 \cdot 12\,SiO_2 \cdot 3\,MgCO_3\,10\,H_2O \begin{cases} 92\,MO = 89\,CaO \cdot 3\,MgO \\ 6\,R_2O_3 = 5\,Al_2O_3 \cdot Fe_2O_3. \end{cases}$

Analysis XXXI.

C. $74\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot 3\,MgCO_3\,8\,H_2O \begin{cases} 74\,Mo = 71\,CaO \cdot 3\,MgO \\ 6\,R_2O_3 = 5\,Al_2O_3 \cdot Fe_2O_3. \end{cases}$

Analysis XXXII.

D. $76\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot MgCO_3 \cdot 4\,H_2O \begin{cases} 76\,MO = 72\,CaO \cdot 4\,MgO \\ 6\,R_2O_3 = 5\,Al_2O_3 \cdot Fe_2O_3. \end{cases}$

Analysis XXXIII.

E. $90\,MO \cdot 6\,R_2O_3 \cdot 18\,SiO_2 \cdot 4\,MgCO_3 \cdot 10\,H_2O \begin{cases} 90\,MO = 86\,CaO \cdot 4\,MgO \\ 6\,R_2O_3 = 5\,Al_2O_3 \cdot Fe_2O_3. \end{cases}$

These results are summarised in the following Table :—

Time	A	B	C	D	E
2 hours	7.53	20.53	9.94	34.01	20.47
6 ,,	10.09	37.05	12.23	35.46	29.57
1 day	18.79	41.35	15.32	38.39	39.78
4 days	—	46.16	29.72	—	—
5 ,,	—	47.17	32.10	—	—
6 ,,	—	57.96	33.56	—	44.34
7 ,,	—	65.63	40.21	—	51.55

Ostwald drew attention to the great increase in heat evolved on the 5th, 6th and 7th days and suggested that after this time a new stage in the hardening process occurs and is accompanied by a fresh development of heat. This noticeable development of heat—for which, hitherto, no satisfactory explanation has been given—is readily understood in the light of the new theory. It is the moment of hydration of the calcium oxide liberated from the silicate molecule.

Further references to the development of heat during hardening will be found in the *Bibliography* under No. 322.

G

As the most important hydraulic limes are aluminosilicates, it must, theoretically, be possible to observe the conversion of primary into secondary types by the action of alkaline solutions of definite concentration. This deduction has been confirmed by some experimental results obtained by Feichtinger[323]. He treated the hydraulic mortars A, B, C and D (both in the fresh state and after they had been allowed to harden for some time)with aqueous solutions of sodium and potassium carbonates, and allowed these reagents to act for some time.

* For the analytical figures, see the corresponding numbers in the section on Portland cements in the *Appendix*.

A definite quantity of silica and a little alumina was dissolved, the amounts being expressed in percentages and molecules in the following Table :

TABLE V

	% SiO_2				Molecules SiO_2			
	A	B	C	D	A	B	C	D
In fresh state . . .	2.63	5.09	6.78	4.24	2.17	4.11	2.98	2.13
After 14 days . . .	1.66	3.72	6.05	2.86	1.34	3.00	2.66	1.90
„ 3 months . .	1.42	2.50	5.80	2.40	1.14	2.02	2.55	1.82
„ 5 „ . . .	1.04	2.10	5.26	2.12	0.84	1.70	2.31	1.65

From this Table it may be seen that the Portland cement A is a basic salt of the type

$$\hat{Si} \cdot \overline{Al} \cdot \hat{Si} \cdot \overline{Al} \cdot \hat{Si}$$

and, in the fresh state, parts with 2 mols. SiO_2, forming

$$\overline{Si} \cdot \overline{Al} \cdot \hat{Si} \cdot \overline{Al} \cdot \overline{Si}.$$

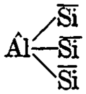
Similarly, the alkaline solution reacts on the hydraulic lime D, which is a compound of the type

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}.$$

It forms a compound of the type

$$\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{Si},$$

and it is interesting to note that the cements B and C, which are both basic salts of the type,



do not, when in the fresh state, part with the same number of molecules.

From B—with the liberation of 4 mols. SiO_2—a compound

$$\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{Si},$$

and from C a salt of the anhydride

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Si},$$

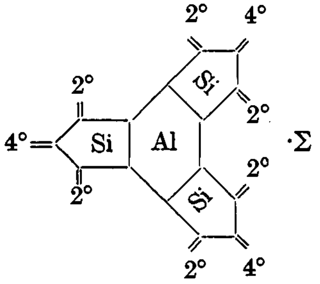
are produced. The last-named shows that hexa-compounds may, in some cases, be produced by the action of alkalies on penta-compounds.

Table V also shows that the solubility of the silica diminishes as the cement mass hardens. This fact is also in agreement with the theory, according to which a separation of CaO from the hydraulites A, B, C and D should occur and the combination between the alumina and silica radicles should be intensified.

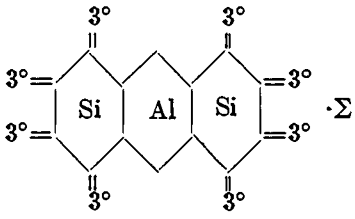
H

The separation of CaO in hydraulic binding materials, which is a result of the action of dilute hydrochloric, sulphuric, carbonic and other acids, of alkaline carbonates or, in some cases, of water alone (Portland cements), must take place in accordance with certain definite stoichiometrical laws. Valuable contributions to the support of this statement have been made by Feichtinger[324] and Schott[325].

Feichtinger has studied the action of water containing carbonic acid on the cements 1(B), 2(C), 3 (A), 4(D) and also on the silicates :



$24\ CaO \cdot 3\ R_2O_3 \cdot 15\ SiO_2 \cdot \Sigma$*
Analysis XX, *Appendix.*
5 (E).



$24\ CaO \cdot 3\ R_2O_3 \cdot 12\ SiO_2 \cdot \Sigma$ †
Analysis I, *Appendix.*
6 (F).

Feichtinger's object was to discover whether the whole of the lime in the hardened material could, in this way, be converted into calcium carbonate or whether this conversion was confined to a portion of the lime. Although he allowed CO_2-water to act on the hardened material for 1½ years, he was unable to convert the whole of the lime into $CaCO_3$; a part of the lime remained combined with the silica. Unfortunately, Feichtinger did not publish the data on which he bases his conclusions regarding the proportions of lime in the free and combined state after 1½ years. The following Table shows the progress of the decomposition, studied by Feichtinger, during only 5 months :

TABLE VI

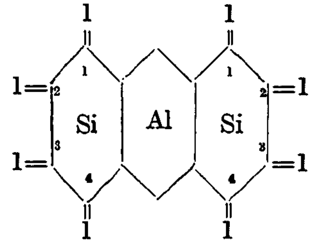
Conditions of Experiments	Percentage of CO_2	
	A	B
The mortar lay 3 months in clean water	4.2	8.1
After this for 1 month in CO_2-water	14.4	16.3
,, ,, 2 months ,, ,, ...	16.7	19.2
,, ,, 3 ,, ,, ,, ...	18.2	19.4
,, ,, 4 ,, ,, ,, ...	20.8	19.4
,, ,, 5 ,, ,, ,, ...	20.9	19.4

* $\Sigma = 4\ RCO_3 + 0.25\ Na_2SO_4 + 2\ H_2O$.
$3\ R_2O_3 = 1.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$.
$4\ RCO_3 = 2.5\ CaCO_3 \cdot 1.5\ MgCO_3$.
† $\Sigma = 3\ RCO_3 + 0.5\ R_2SO_4 + 2\ H_2O$.
$3\ R_2O_3 = 1.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$.
$3\ RCO_3 = 2\ CaCO_3 \cdot MgCO_3$.

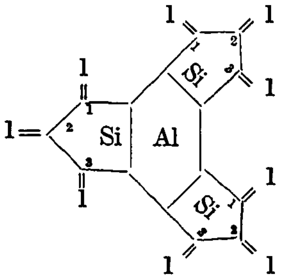
TABLE VII

% CaO (calculated)	% CaO (found)	% CO_2 taken up by the mortar in 5 months	Mols. CO_2 taken up by the mortar in 5 months	Mols. combined CaO in fresh mixed mortar	Mols. combined CaO after 5 months	Theoretical amount of CO_2 in %	Molecular Weight of Mortar	Classification (after F.)	Free lime in the freshly mixed mortar	Total Mols. CO_2 in Mortar
41.36	40.90	22.5	16	24	8	23.45	2860.8	F	0	19.0
38.12	36.13	19.4	12	21	9	19.30	2777.4	B	0	14.5
37.48	37.10	21.2	16	22	6	21.59	2659.4	C	0	16.5
39.56	36.80	21.3	15	24	9	22.29	3090.9	E	0	19.0
43.84	42.30	20.9	26	44	18	22.27	4585.0	A	0	29.0
41.13	41.70	24.0	27	26	12	23.14	4327.0	D	13	29.0

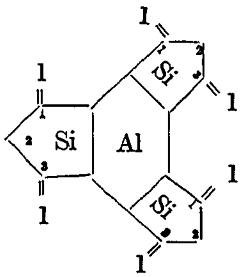
Table VII is of special value, as it allows the inference that the following products have been formed by the action of carbonic acid on the hydraulites F, B, C, E, A and D :



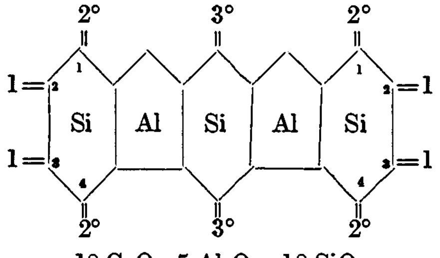
$8 CaO \cdot 3 Al_2O_3 \cdot 12 SiO_2$
F.



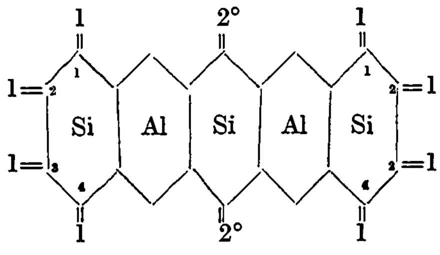
$9 CaO \cdot 3 Al_2O_3 \cdot 15 SiO_2$
B and E.



$6 CaO \cdot 3 Al_2O_3 \cdot 15 SiO_2$.
C.



$18 CaO \cdot 5 Al_2O_3 \cdot 18 SiO_2$
A.



$12 CaO \cdot 6 Al_2O_3 \cdot 18 SiO_2$
D.

A glance at the above structural formulæ shows that the separation of CaO must be in accordance with quite definite laws. Hence it follows from the structural formulæ A and D that :

1. The lime is combined more strongly with the middle hexite and cannot be so easily separated as it can from the side hexites, and

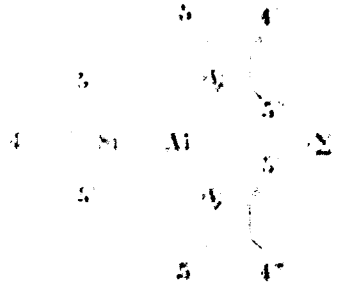
2. In the neighbouring positions 2 and 3, the lime is more feebly bound than in the positions 1 and 4.

It appears to be unlikely that the 2° side-chains in the compound A are in neighbouring positions (2, 3).

A comparison of the structural formulæ B, C and E shows that the lime in positions 1 and 3 in the pentites is more strongly combined than in position 2. The possibility that the lime in C forms a 2° side-chain in position 2 is improbable.

Schott[338] studied the reaction of a cement:

$$42\,CaO \cdot 3\,R_2O_3 \cdot 15\,SiO_2 \cdot \Sigma^*.$$



Molecular Weight = 3974.4

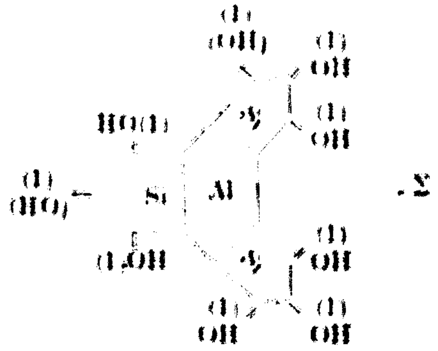
G.

137.4 parts of cement hardened by $(NH_4)_2CO_3$ gave:

$CaCO_3$	$MgCO_3$	$CaSO_4$	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Insol.	Total.
79.20	2.90	1.30	15.10	4.30	4.50	22.70	6.10	1.30	137.40
57.50	2.10	0.98	10.90	3.14	3.28	16.53	4.44	0.98	100.00%

These results lead to the formula:

	11 CaO	Fe_2O_3	2 Al_2O_3	15 SiO_2	31 $CaCO_3$	1.5 $MgCO_3$	0.5 $CaSO_4$	14 H_2O
Calcd.	11.34	2.05	3.75	16.68	57.00	2.32	1.25	4.64
Found	10.99	3.14	3.28	16.53	57.50	2.10	0.98	4.44
							0.98 (Insol.)	



$$(9\,H_2O \cdot 9\,CaO \cdot 3\,R_2O_3 \cdot 15\,SiO_2)$$
$$+ 32.5\,RCO_3 + 2\,Ca(OH)_2 + 3\,H_2O + 0.5\,CaSO_4$$

H.

* $\Sigma = 2.5\,RCO_3 \cdot 0.5\,CaSO_4 \cdot 2\,H_2O$
$2.5\,RCO_3 = 1.5\,MgCO_3 + 0.5\,K_2CO_3 + 0.5\,Na_2CO_3$.
$3\,R_2O_3 = 2\,Al_2O_3 \cdot Fe_2O_3$

The structural formula H suggests a comparison with the formula B previously given. The decomposition, so far as the separation of lime is concerned, occurs in a similar manner; this can scarcely be a mere coincidence.

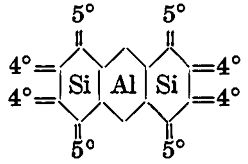
More hydration phases occur under the action of alkaline carbonates of certain concentration than with water alone. Hence, in such cases, the cement masses must attain a greater hardness, as Schott has shown experimentally.

It is, therefore, very important to ascertain the nature of the action of carbonic acid on hardened mortar, as a clear conception of the changes which occur to cement mortars hardening in air may then be obtained. The secondary hardening of cements allowed to set in air must be chiefly referred to the action of carbon dioxide and moisture in the air.

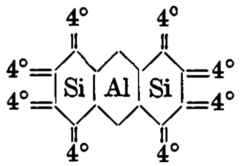
As the cement mortar, in such a case, undergoes a large number of hydration phases which follow each other very slowly, storing in air ought to give a harder product than is obtained by storage underwater.

J

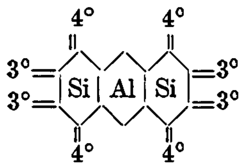
In a hydraulite of the composition



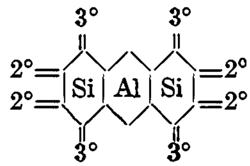
it is possible to remove a portion of the lime by means of hydrochloric, carbonic or other dilute acids, or of dilute ammonium carbonate solution. The following compounds may be produced in this manner:



1.



2.



3.

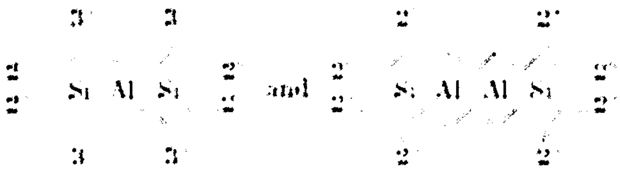
etc.

These compounds may, in the presence of water or dilute alkalies, undergo a series of hydration phases. Hence, if a portion of the lime is removed from combination with the cement by means of dilute acids, it must, to a certain extent, retain its hydraulic properties.

Fremy[327] has experimentally removed a portion of the lime from hydraulic limes, and has treated the residue with dissolved lime, with the result that the mixture hardened. Zulkowski[328] repeated Fremy's experiment, and found that as much as 14 per cent. may be removed from some Portland cements without destroying the power of the residue to harden when mixed with water.

K

Such hydraulites as



A. B.

cannot contain more than 8 molecules of silicate-water, but, in addition to this, A can have a theoretical maximum of 20 $Ca(OH)_2$, or 20 H_2O which is driven off at a red heat. B, under similar circumstances, cannot have more than 16 mols. $Ca(OH)_2$, or 16 H_2O volatilised at a red heat. In other words, there is for each cement molecule a maximum proportion of silicate-water and of calcium hydroxide water. This statement is also true of all analogously constituted silicate cements.

It will be interesting to observe how far this inference from the theory is supported by the facts.

L

If a hardened mass of cement containing free basic lime-salts is crushed, it will harden into a stony mass if mixed with a suitable quantity of water or dilute solution of alkali. These lime-salts are particularly likely to be present where hydration is effected by the action of alkali-free or acid-free water. As the number of hydration phases in such partially decomposed silicates is large, especially in the presence of a little alkali and water, it should be possible to produce materials or articles of great hardness from such silicates.

Schott[219] has experimentally obtained a second setting and hardening by mixing a pulverised hardened cement mass with water.

M

As the bond between the aluminium hexite and the silicon hexites is weakened by heating aluminosilicates and by their combination with lime, it should be possible to observe that when the material is treated with dilute acids, a separation of lime and of gelatinous silica occurs, as in clays (p. 107).

This is actually the case, and Fuchs made this fact the basis of his cement theory.

N

If hydraulic limes are treated with concentrated hydrochloric, sulphuric, or other acids, it should be possible to observe a decomposition of the silicate molecule in addition to the separation of the

lime. The silicate molecules, being derivatives of clays, must be resolved into compounds of the type

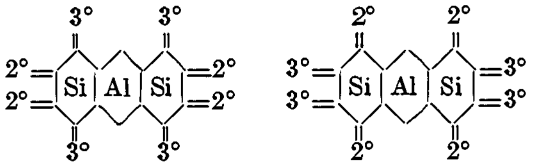
$$\hat{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\hat{Si},\quad \overline{Si}\cdot\hat{Al}\cdot\hat{Al}\cdot\overline{Si},\quad \text{or}\quad \hat{Si}\cdot\overline{Al}\cdot\overline{Al}\cdot\hat{Si}$$

(see p. 107).

So far as the authors are aware, no experiments to prove this have yet been made.

O

From the theory, the possible existence of isomers of the silicate cements may also be inferred. Thus the compounds



are isomeric. Up to the present these isomers have not been investigated.

P

Good hydraulites ought only to be producible by mixing hydroaluminosilicates (clays) with limestone or chalk in theoretical stoichiometric proportions, the ash of the fuel (alumina, silica, lime and alkali) used being also taken into consideration.

As a matter of experience it is well known that for each mixture only definite proportions of clay and lime can be used to produce good cements. These proportions are usually found empirically, but the formulæ given by the authors show that these empirical proportions agree with the ones theoretically the most suitable and that the empirical proportions are scientifically correct.

Q

A New Investigation of the Sea Water Question

Schuljatschenko[330] correctly states that it is very difficult to ascertain accurately the cause of the destruction of masonry exposed to the action of the sea; i.e. whether it is due to the properties of the bonding material (cement), to external influences such as sand, to incorrect proportions of the materials used in the concrete, to the porosity or to the low density of the cement blocks, etc. There can be no doubt that all these factors have some influence, but the facts seem to show that, in many cases, the chief cause of the decomposition of maritime masonry is the action of sulphur compounds. That this inference is generally true is shown by the fact that a large number of

investigators have, for many years, endeavoured to ascertain what substances are formed by the action of calcium sulphate on cements.

It is generally agreed that Portland cements contain compounds of lime and alumina, and Candelot[331] and Michaelis[332] have concluded that, by the action of gypsum or plaster of Paris on hardened cement masses, certain calcium sulpho-aluminates are formed, and that these are one of the causes of swelling of cements. Schott[333] also investigated the action of gypsum (plaster of Paris) on normal Portland cement and on analogous cements in which the alumina is replaced by iron oxide. In both cases he noticed that decomposition occurred, so that the formation of a calcium sulpho-aluminate or sulpho-ferrate appears to be probable. Schott did not, however, agree with the investigators just named that the swelling action of gypsum (plaster) is due to the formation of sulpho-aluminates or sulpho-ferrates. Le Chatelier[334], on the contrary, is in favour of the formation of a definite calcium sulpho-aluminate and, like Deval[335], endeavoured to ascertain the action of various sulphates on cements containing various proportions of alumina.

Rebuffat[336] also found that there is a number of different calcium sulpho-aluminates. He doubted, however, whether the destruction of maritime masonry could be referred to the formation of these compounds. Here again, it should be noticed, the swelling and disintegrating effects which occur when gypsum (plaster) is present in the cement were also attributed to the last-named substance. The chief description of the disadvantages of sulphates on cements is that of Schiffner[337], who had collected a number of instances in which the decomposition was unquestionably due to the action of sulphur compounds on the hardened cement masses. Some of these interesting examples may be mentioned here :

1. In the walls of a railway tunnel, the effects of some destructive action were observed. The mortar came out of the joints in the form of a milky fluid and carried with it all the sulphate, so that the cement was considered to be bad. It was only after a very careful examination that it was found that the overlying rocks contained sulphurous lignite which became oxidised to sulphates, the latter causing the destruction of the cement.

2. In a concreted gallery in a mine in Alsace-Lorraine the walls became moist and porous in parts. The greater portion of the structure was in exceptionally good condition, so that it was impossible to blame the cement, but in some portions boil-like swellings appeared, the mortar becoming semi-fluid and the joints loose. A closer examination showed that the nature of the water in the neighbourhood of the gallery contained calcium and magnesium sulphates in sufficient quantities to effect a partial decomposition of the concrete.

3. According to Grauer, cracks and characteristic white crystals

appeared in the joints of a sewer built of bricks laid in cement. In this instance the sulphates were introduced by the sewage.

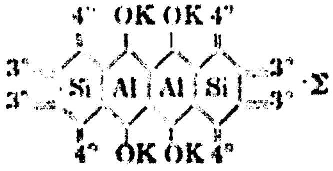
4. According to Le Chatelier, defects appeared in the cement used in the Paris fortifications because this was quite close to the famous gypsum beds. In this instance the sulphuric acid in the cement rose from 0.4 to 3.75 per cent.

5. In a tunnel near Almeria (Spain) the mortar swelled a few months after it had been finished. The sulphuric acid content rose from 0.3 to 2.3 per cent. The ground water contained 2 g. calcium sulphate and 1½ g. magnesium sulphate per litre (or 140 and 105 grains per gallon respectively).

6. A railway viaduct, which passed through a clay deposit containing gypsum and through gypsum beds, suffered seriously because the drainage water was saturated with gypsum.

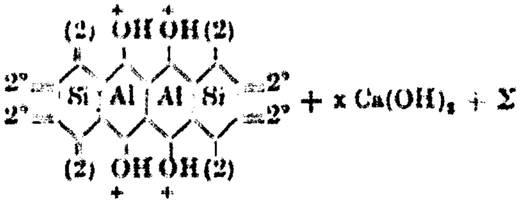
These instances are sufficient to show the serious action of sulphur compounds on cement, and the question arises as to whether any information may be gained from a study of the constitution of the cements, or from the observations and experiments which have been made, whereby this action may be explained, and, if possible, prevented. The reader may be surprised to learn that this question can be answered in the affirmative in the following manner:

If water is allowed to act on a typical Portland cement such as:



A.

a hard, cement mass with the formula



B.

is formed.

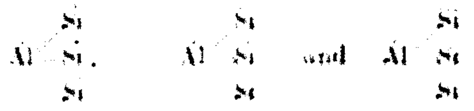
From the formula B it may be seen that the silicate of the hardened cement contains *a*-hydrogen (marked with a +), and on p. 140 it was shown that the *a*-hydrogen tends to be replaced by monovalent acid radicles such as $-SO_2 \cdot OH$, $-SO \cdot OH$, etc.

In this manner all kinds of *A*- and Σ-aluminosilicates such as the ultramarines (p. 140 *et seq.*) may be formed. If the cement mass B comes into contact with solutions of salts such as gypsum, it is by no

means improbable that Σ-aluminosilicates will be formed. High temperatures are unnecessary, as Thugutt has shown that the formation of the Σ-aluminosilicates (sodalites) may take place at low temperatures in the presence of solutions of suitable salts. As the formation of these substances is accompanied by a change in volume, it is clear that the hardened cement, such as B, must crack if its hydrogen is replaced by acids or acid radicles (p. 152) and that it may be completely destroyed.

Hence it follows that the authors' cement theory permits the prediction that the action of sulphates on cement will be accompanied by disastrous results. The possibility of the disintegration of maritime masonry by the action of the sulphates of calcium, magnesium, etc., in the sea water is thereby explained.

There now remains the question as to whether this serious action of sea water can be, in any way, prevented. In cases where the destruction of the cement work is exclusively confined to the action of the sea water, the most satisfactory solution of the problem will be found in the use of cements in which no a-hydroxyls can be formed, i.e. cements of the types

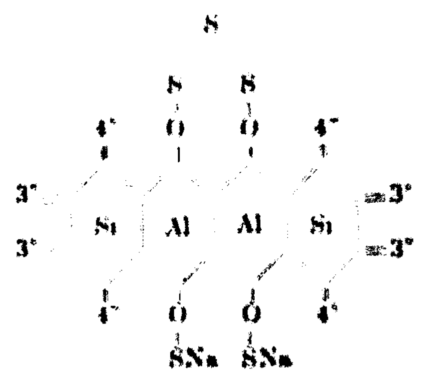


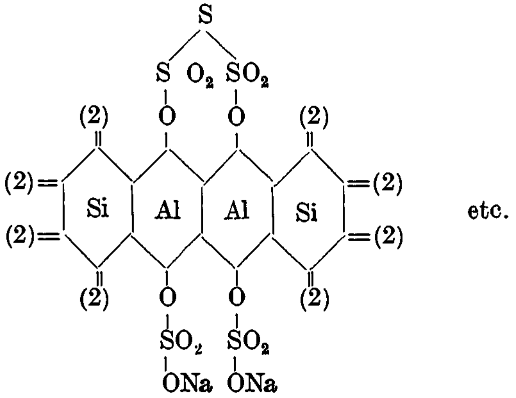
(p. 189)

If this inference from the theory can be proved experimentally—and the practical observations and experimental results previously mentioned almost amount to such a proof—an interesting and important practical result would be obtained from purely theoretical reasoning, and would form a notable step in the direction of a solution of the "sea-water problem."

II

From the theory it follows that, from clays containing a-hydroxyls, compounds must be producible which contain both hydraulites and A- or Σ-aluminates or ultramarines, i.e. pigments with hydraulic properties such as:





It will be interesting to learn whether this prognosis can be proved by the actual production of such substances.

XIV

A New Theory of the Silicate or Porcelain Cements

Certain kinds of transparent silicate cements, which are conveniently known as porcelain cements, have been used for some years as dental-stopping materials. The first of these porcelain cements was discovered and patented in 1878 by T. Fletcher[338], but it did not fulfil his anticipations and rapidly fell out of use.[339] An interval of 25 years appears to have elapsed before any other porcelain cements were produced, and these were of a different composition. Those placed on the market in 1904 by Ascher and others were heartily welcomed as new discoveries in dentistry, and they rapidly attained great popularity on account of their valuable characteristics.

It may be here pointed out that the porcelain cements appear likely not only to replace the zinc phosphate cements and amalgams, but also the burned enamels and the " queen " of stoppings—gold—in practical dentistry ! Morgenstern has expressed himself as follows respecting these new stopping materials : [340] " Porcelain cement, when properly selected and prepared, sets to form a mass with a remarkable resemblance to natural teeth, both in colour and transparency and possessing a gloss which is confusingly like that of natural dentitic enamel. These stoppings have no objectionable features, and in no way harm the teeth, and they have a great advantage over gold and the burned enamels in that they save the dentist thousands of hours of work and greatly economise his health and power. They save the patients many a painful hour and have great pecuniary advantages."

Porcelain cements consist of two ingredients—a powder and a fluid. According to Sanderson, Fletcher's powder was composed of aluminium hydrate, zinc oxide or magnesia and a basic zinc silicate. The powders

of the new porcelain cements consist chiefly of calcium aluminosilicates.

The fluids of the new cements differ from that of Fletcher chiefly in their consistency. Fletcher's fluid was a syrupy solution of aluminium phosphate in phosphoric acid, whilst the newer ones are less syrupy and consist chiefly of alumina and phosphoric acid. There was, until recently, a cement of which the powder resembled that of Fletcher and consisted chiefly of calcium aluminosilicate and zinc oxide. The fluid had a consistency resembling that of Fletcher's fluid, but was chiefly composed of alumina and phosphoric acid with a large proportion of zinc oxide. It differed from Fletcher's cement because it was a practicable, dental-stopping material.

On mixing the silicate powder with the fluid, there is immediately formed a transparent mass which is at first plastic—in distinction from the earlier zinc phosphate dental cements—but rapidly becomes quite hard.

The powder of the new cements contains the same constituents as the Portland and slag cements, but instead of the fluid being pure water or alkaline water, acids (aluminophosphoric acids), or solutions of acid salts (aluminophosphates), are employed.

From a scientific point of view it is highly important that an investigation should be made with a view to ascertaining the constitution of the porcelain cements in order to solve a number of physical and chemical problems in connection with their setting. This investigation appears to be all the more necessary when the available experimental results and the theories already formulated are critically examined. If the new hexite theory proves of use in this investigation, it will not only add to the value of the theory itself, but will clear many problems of enormous and pressing importance in surgery and particularly in dentistry.

The new silicate cements—with the exception of those containing a large proportion of zinc oxide both in the powder and in the fluid portion—have one serious drawback : they have a destructive action on the nerves (*pulpa*) of the teeth. For this reason there has long been a dispute as to the best means of preventing this poisonous action.

In regard to this and to several other problems—e.g. the best methods of testing the durability, density and hardness of such cements, both in the laboratory and in the mouth—much remains to be done. It is, however, clear, that in all investigations of this kind, a knowledge of the constitution of the cements and of the changes which take place during their setting, must be of the greatest importance.

The porcelain cements must possess a number of very definite characteristics, such as unchangeableness of shape and size in the mouth, resistance to the action of saliva, etc., if they are to fill a useful place in applied dentistry.

Miller[341] considers that an ideal dental stopping should have the following characteristics :

1. Sufficient hardness so as not to be worn away unduly by mechanical forces in the mouth.

2. Unchangeability in saliva, food-stuffs and other decomposition products (chemical indestructability).

3. Constancy of form and volume when placed in the teeth.

4. Low heat conductivity, so that any changes in the temperature of the mouth are not transmitted to the nerves of the teeth.

5. A high degree of plasticity in order that the stopping may be water-tight and may properly fit the teeth.

6. Colour as similar as possible to that of the teeth.

7. Absence of detrimental action on the tooth material, nerves, mucous membrane and the general health.

8. Easy manipulation.

9. Minimum sensitiveness to moisture.

10. Adhesiveness to the tooth-wall.

11. Antiseptic, at any rate during fitting.

12. Easy removal, if necessary.

The possibility of producing ideal stopping materials depends chiefly on a knowledge of the chemical constitution and on a clear understanding of the reaction which occurs during the hardening of these substances. If no scientific basis—no scientifically grounded theory—of the porcelain cements is possible, the manufacturers of these substances can only work in an *arbitrary* manner in attempting to improve the quality. To do this is, however, risky, as it is possible that some manufacturers may even produce *inferior products* instead of "improvements"; the final material may, in fact, be worse than the original one, though it may be sold as "greatly improved." In one case a porcelain cement was so much "improved" that it was eventually agreed that the material made five years previously was by far the "best," and the manufacturers were obliged to forego their "improvements" and to use the older recipe !

A large amount of theoretical, and especially of experimental work, has been done in connection with porcelain cements, but it cannot be said that this has made the most important properties, such as the poisonous nature of some of these cements, more comprehensible. The solution of this problem of poisoning—undoubtedly one of the most important—is made particularly difficult by the absence of any well-established theory, and even more serious are the effects of false and purely speculative theories and especially of wrong explanations and faulty interpretations of experimental results.

In this connection the litmus experiment of Rawitzer[348] is peculiarly typical. This investigator endeavoured to show, by means of strips of paper soaked in blue litmus solution, that the porcelain cements containing zinc oxide are poisonous, whereas their innocuousness has been proved by laboratory tests and is obvious from a study of their chemical constitution. Rawitzer appears to have overlooked the fact that a substance may turn blue litmus red and yet may not be

prejudicial to health ; it all depends on the amount of acidity present. A substance may even be acid and yet may not have any detrimental action on the teeth. For instance, *concentrated* hydrochloric acid is unquestionably a violent poison, but dilute hydrochloric acid is, on the contrary, an internal medicine of great value. Yet both solutions turn blue litmus red ! Litmus alone cannot give any clue as to the amount of acidity, and is, therefore, useless for determining poisonous qualities. Rawitzer had not, apparently, a clear view of the meaning of the term "acid reaction," and was but partially informed with regard to the structure of the hardened cement masses ; consequently he had an erroneous idea of the physico-chemical reactions occurring during the hardening.

The absence of more definite knowledge of the nature of the porcelain cements has led to several false and meaningless investigations by Dreschfeld[342], Strümpel[343], Robert Richter[344], and Kulka[345]. These have been criticised by Schreiber[346].

For instance, Dreschfeld, Strümpel and Richter[347] digested the raw cement (composed of a solid aluminosilicate and a fluid containing alumino-phosphoric acid and aluminophosphate of zinc) with water for various periods of time. According to the length of this digestion a proportionate quantity of the uncombined cement would be decomposed, the result being a partial splitting up of the cement mass into its components. These acid-reacting decomposition products were titrated and regarded as "free phosphoric acid" by the investigators named.

Yet what is the use of showing the presence of acid in the decomposition products of a substance which is known to have an acid as one of its original constituents ?

The same authors also studied the action of freshly mixed (and therefore uncombined) cements on various colourless solutions as well as solutions of aniline dyes, fruit juices (bilberry juice), etc. They regarded a cement which produced no colour in the presence of aniline dye-stuffs as perfect ! Yet it is clear that even the "densest cement," in a fresh (unhardened) state, must necessarily form a compound of an intense colour if such cements form a lake by combining with the dye-stuff. It is a well-known fact that a valuable series of aniline lakes are produced from aluminosilicates and certain basic aniline dye-stuffs ; is it reasonable to suggest that, because an aluminosilicate forms a lake with a certain aniline dye-stuff, it is, therefore, unsuitable as a dental stopping ?

Kulka falls into a similar error in his experiments, and he appears to have paid no attention to the physico-chemical reactions of hardening in his studies, although Morgenstern[349] and Schreiber[350] had called attention to them. Morgenstern was, therefore, induced to issue a warning in regard to the experiments of Kulka and to the general manner in which investigations on silicate cements are carried out. In this warning Schreiber joined. Both these authorities believe that it may be safely assumed that Kulka would never have carried out

his experiments on imperfectly hardened cements if he had been clear as to the constitution of these substances and the changes in their physical and chemical properties which occur during the different hardening phases.

As Morgenstern[351] rightly says : " It is incorrect to stop the various chemical and mechanical processes in cements prepared for experimental purposes before the hardening is complete. The cements so treated lose very valuable properties and lead to erroneous results.

" If this were a matter of purely theoretical or academic interest I should not write about it, but would modestly express my contrary opinion. This is, however, a case where the conclusions are of great practical and technical importance, and Kulka's theories may have a most important influence on the use of silicate cements in dentistry and on their production by the manufacturers. It is because I am convinced that this influence may be profitless and even harmful that I feel right to call ' Halt ! ' to those colleagues who are following these new paths."

Morgenstern himself treated the cements with chemical agents from half to three hours after hardening. He agrees, however, that he could not, in this way, definitely ascertain the true properties of the cements he examined : " I treated," he says,[352] " my cements with water at 35° C. for one-half to three hours, and found that their adhesion, durability, density and resistance to acids and alkalies were such that the results obtained cannot be regarded as showing the inherent good characteristics or their value as dental stoppings."

Morgenstern[353] rightly says that in many of his experiments Kulka paid too little attention to the time required for hardening the cements : " Before commencing his special experiments, he (Kulka) treated his cement fillings (30 minutes after they had set) with a mixture of saliva and water and allowed them to remain in it for seven days, the fluid being renewed occasionally. He found that some cements showed no change, others a little change, and others again were much altered, and that one cement was completely destroyed. These changes in structure and hardness are good evidence that the different cements take different times to complete hardening."

As Kulka, in his researches, did not pay any attention to the hardening phases in his cements, he found, as Morgenstern has shown, that as great a loss of material occurred when the cement was treated with a 0.5 per cent. solution of lactic acid as is only produced in three weeks in a properly hardened cement.

Schreiber[354] has pointed out the interesting fact that Kulka's phosphate cements possessed no adhesion, so that Kulka's conclusions —based on too early a treatment of the cements with saliva, i.e. before they had properly hardened—must, necessarily, be erroneous. As a matter of fact, Kulka covered the ends of small pieces of ivory with cement, and after an hour's standing placed them in saliva-water, where they remained for six days. At the end of this period he found " to his

astonishment" that the ivory could be completely withdrawn from the cement covering with comparative ease. From this experiment Kulka drew his erroneous conclusions.

Another serious omission in the records of experiments mentioned on the last two pages is that none of the investigators named mentions the proportion of powder to fluid which he used in his tests. Hence it is not difficult to understand that, as Schreiber[355] has shown, under apparently identical conditions a cement mass x is, according to one investigator, only $\frac{1}{34}$th as resistant as the mass y; according to another investigator it is only $\frac{1}{6}$th as resistant as the same mass y; according to a third it has the same resistance to acids as y, and, finally, a fourth reports it as being more resistant than y! Clearly, these different men have worked with cements of widely differing degrees of hardness and therefore with very different proportions of powder to fluid. Schreiber has correctly stated, in regard to this remarkable result of the study of these experiments with silicate cements: "Are not these results significant? Can any reliance be placed on experiments which give such contradictory results? It is impossible to believe that any substance can behave so differently in analogous experiments."

In spite of Morgenstern's warning and Schreiber's severe criticism, Kulka has continued to pay no attention to the hardening phases and other important properties of the silicate cements. In his latest work —on the possibility of chemical and pathological actions of cement stoppings[356]—he endeavours to determine the acidity of various silicate masses shortly after they have been produced, i.e. during the first stages of hardening. This is a very important problem; yet how does Kulka attempt its solution? He mixes the powder with the fluid and, either at once or after 20 to 40 minutes, during which the mass is kept at a temperature of 35°, he grinds it to a fine powder. He then treats about 1 g. of this powder with 150 c.c. distilled water for 24 to 48 hours. At the end of this period the powder is removed by filtration and the liquid titrated with $\frac{n}{100}$ potassium hydrate. The alkali neutralised is expressed in terms of "free phosphoric acid."

A further study of this so-called "quantitative determination" of the "free phosphoric acid" shows that this method is not merely objectionable, but is *entirely erroneous* because:

1. By adding a larger quantity of water to the finely powdered but unhardened cement mass, and especially if it is also stirred continuously for 24 to 48 hours, not only is the cement decomposed, but, in the case of cements in which the fluid is a solution of zinc salts, these salts separate out as new constituents! Acid decomposition products of the most varied nature enter partially into solution. On titrating the filtrate—assuming that it can be titrated (see 2 below)—what is really determined is the proportion of substances which are, to a large extent, of *secondary* origin and *are not contained in the original material!*

2. It is entirely wrong in principle to titrate acid-reacting solutions of metallic salts (zinc salts of aluminophosphoric acid) and to determine the "free acid" by means of the amount of potassium hydrate required, because many solutions of metallic salts react like acids, but *contain no trace of free acid.* Copper sulphate, cobalt chloride, nickel sulphate, etc., are typical in this respect.

3. None of the fluid portions of silicate cements contained free phosphoric acid, but phosphoric acid combined with alumina, i.e. aluminophosphoric acid and their zinc salts.

These complex aluminophosphoric acids and their salts have entirely different chemical and physiological properties from those of free phosphoric acid and must not be confused with it. This is the more important as the alumina, as will be shown later, plays a very important part in the physiologico-chemical action of these acids.

Yet Kulka, in his determination of the "free acid," entirely overlooks this alumina and regards the cement fluid as consisting of "orthophosphoric acid" in which one atom of hydrogen has been replaced by a base. This view is quite erroneous and unfounded.

Under these conditions it is not surprising that Kulka's "determinations of acidity," in various silicate masses, led him to regard what are known in practice as *highly poisonous* cements as "harmless" and those which are entirely free from danger as "the most poisonous."

From the experiments of Morgenstern, Kulka and others it was discovered that the porcelain cements have a far higher resistance to acids than have ivory[357] and the enamel of natural teeth.[358]

This fact is of special importance inasmuch as it provides the key to the constitution of the silicate cements. It is also important to observe that some of these cements possess this high resistance even before they are fully hardened! This fact also provides means for studying the course of reactions which occur during the hardening and in this way excludes *a priori* a number of hypotheses which will be mentioned presently.

Critical Examination of various Hypotheses concerning the Course of Reaction during the Hardening of the Porcelain Cements

Experimental results are available from which it is possible to learn the course of the chemical reactions which occur in the hardening of porcelain cements. It is clear that so long as no scientific and well-founded theory was put forward, these results must remain in the background. Several of these hypotheses must, however, be abandoned, if the high resistance of the half-hardened cement to acids is to be taken into consideration.

Jung[359] was one of the first to endeavour to explain the chemical changes which result in the hardening of the porcelain cements. He first assumed that the powders are "chemical compounds of silica, alumina, lime," etc., but found an "important error" in the composition of these cements and was led to conclude that, on mixing the

powder with the fluid, a separation of lime and magnesia in the form of calcium and magnesium phosphate—i.e. a separation of readily soluble substances—must occur. "The solubility of these substances in acids," says Jung, "may be reduced by the admixture of alumina, silica, etc., but it can never be removed altogether."

The proved slight solubility of the porcelain cements in acids is clearly opposed to the separation of lime and magnesia as just suggested.

Morgenstern[360] also appears to have discovered the same "important error" as Jung. "We know," he says, "that the general chemical composition of the cements is due to their calcium and magnesium contents, and that the reaction between the powder and the fluid results in the formation of calcium and magnesium phosphates, which are known to be readily soluble in acids. This naturally leads us to fear that dental stoppings made of such cements cannot have much resistance to the acids present in the human mouth." Yet Morgenstern has, himself, shown the great resistance of these cements to acids, and has further demonstrated that the reactions which take place during hardening must be different from those mentioned in the above quotation.[357,358]

Kulka[361], in 1909, published a theory concerning the chemical reactions occurring during the hardening of porcelain cements, according to which the action of the acid on the powder produces successively primary, secondary and tertiary calcium phosphates. This theory is, however, opposed to the resistance of the silicate masses to acids which Kulka has, himself, proved!

Schreiber[362] has severely criticised Kulka's theory, and has rightly demanded that any theory of the hardening of a cement must necessarily explain why the calcium compounds produced do harden. Any theory to be satisfactory must, for example, explain why a cement fluid which has been diluted with water effects a more rapid hardening than the concentrated fluid, and so forth. For this fact the Kulka theory affords no explanation.

Rawitzer[363] has also attempted to explain the course of the reactions which produce a hardening of the porcelain cements; but his suggestion that the phosphoric acid in the cement fluid causes the precipitation of the whole of the silica in the aluminosilicate powder in an insoluble form is directly opposed to general experience with regard to the behaviour of aluminosilicates. Moreover, silica precipitated in an insoluble form from aluminosilicates must usually be in the form of a gelatinous mass, yet in porcelain cements this form is not produced.

Somewhat more noteworthy is the hardening theory suggested by Apfelstädt[364], who considers the powder to be composed of a mixture of alumina and clay. On mixing this powder with the fluid, the alumina combines with the "free phosphoric acid" in the latter, $Al_2(PO_4)_2$ being precipitated. This precipitate "cements the previously formed

aluminium phosphate and the clay substance together." This investigator also attributes the poisonous action of the silicate cements to the presence of "free phosphoric acid." His theory affords no explanation of the great resistance of the fully hardened cements to acids. It is well known that clay substance is resistant to acids, yet the alumina and the "cemented aluminium phosphate" must be readily soluble in acids. What, also, is to be said about the lime and magnesia? To this question, Apfelstädt's theory affords no answer. Moreover, the expression "cemented" is by no means a clear one. In short, Apfelstädt gives no satisfactory explanation of hardening, and his opinion that porcelain cements are mixtures of alumina and clay substance is without foundation.

From the foregoing pages it will be readily understood how feeble and unsatisfactory are the theories criticised and that the investigations hitherto made have led to no results of importance. Hence there are reasons for supposing that an application of the H.P. theory of silicate constitution to the hardening of porcelain cements is not without interest.

Before attempting this, however, it is desirable to enquire whether the porcelain cements, as such, are single chemical compounds, as it is only then that they can be elucidated in the light of the silicate theory.

As the result of numerous investigations made by them in the manufacture of porcelain cements and of their studies of such cements as are now obtainable commercially, the authors of the present volume have reached the conclusion that these substances are really single chemical compounds, chiefly calcium aluminosilicates.

The chief reason for supposing them to possess this unitary character is the manner in which they are produced: useful cements can only be made from clays (hydro-aluminosilicates) and lime or other bases mixed in definite stoichiometric proportions and heated to redness.

It is also impossible to separate a porcelain cement into different ingredients by mechanical treatment, such as washing with an inert fluid. Such fractions as are obtained in this manner all have the same composition.

The unitary character of these compounds is confirmed by the following:—It might be supposed that the silicate powder is composed of mixtures of calcium aluminate and calcium silicate or calcium aluminate and aluminosilicate, or of silica, calcium aluminate and aluminosilicate. These constituents could then be readily separated on account of their different specific gravities. But no such separation is possible! The high resistance to acids of such mixtures in the form of half-hardened cements, as found by Morgenstern and Kulka, would be inexplicable. The contrary is really the case! Furthermore, the presence of some constituents, such as calcium aluminate or calcium silicate, is thereby excluded, as these products, even after being heated

to redness, readily absorb CO_2 from the air. On mixing a given porcelain cement with the cement acid an evolution of CO_2 should therefore be observable, but this is not the case.

The objection may be raised that a study of the Patent Specifications leads to the conclusion that many porcelains cannot be single compounds. Thus O. Hoffmann (German patent No. 199,664, Kl. 30h of 7th April, 1907) claims a "Method of producing dental cements characterised by the use of aluminosilicates alone or in admixture with other substances."

A suggestion of the non-unitary character of porcelain cements is also given in Rawitzer's German patent, No. 196,510, Kl. 30h of 20th November, 1905, in which he claims "the production of a dental cement-powder for transparent dental stoppings which is to be mixed with phosphoric acid before use." This powder is made by "mixing heated but unfused aluminium silicate Al_2O_3 SiO_2 with a previously melted mixture of calcium aluminum oxide and silica."

The study of commercial porcelain cements made by the manufacturers previously indicated show beyond all doubt that their dental cements were not made according to this recipe! For instance, a "cement" which contained a large proportion of precipitated aluminosilicate was entirely useless as a dental cement on account of the ready solubility of the precipitated aluminosilicate in acids, and the ready decomposition of the "cement" by acids. The ordinary porcelain cement made by the same manufacturer is, like all other cements of clay, very resistant to acids, so that these cements cannot contain a large proportion of precipitated aluminosilicate.

There is no doubt that the various porcelain cements do contain admixtures of salts (basic and acid) and, possibly, small quantities of precipitated aluminosilicate, these being added to give certain definite characteristics to the material and to regulate the time of setting and hardening.

It is also well known that only in the rarest cases are the recipes in the Patent Specifications correct for making commercial products. For instance, the patentee of the well known Rostaing cement was the first to use zinc phosphate for dental purposes. Yet Rostaing was, after Jung's[365] recommendations, so careful and took such pains to express himself so broadly and in such an incomprehensible manner that it has not, so far, been found possible to produce a cement having all the properties possessed by Rostaing's own preparation by following the directions in the Patent Specification.

Hence the Patent Specifications cannot be regarded as being opposed to the unitary nature of the porcelain cements.

A physico-chemical Theory of the Hardening of Porcelain Cements

In formulating a theory of the hardening of porcelain cements, the following matters must receive special attention:

(*a*) The chemical constitution of the porcelain cements.

(*b*) The attraction of aluminosilicates for acids and bases.*
(*c*) The physico-chemical progress of the hardening.

(*a*) The Chemical Constitution of the Porcelain Cements

It has already been shown that a hydro-aluminosilicate of the formula

$\overset{\bullet}{H}_{20}(\dot{Si} \cdot \dot{Al} \cdot \hat{Al} \cdot \hat{Si})$

contains two kinds of hydroxyls: *a*- and *s*-hydroxyls; the former playing the most important part in ultramarines and the latter in Portland cements.

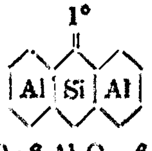
In Portland cements the hydrogen of *s*-hydroxyls—the *s*-hydrogen—may be substituted by monovalent basic groups, viz. R″ · OH, —R″ · O · R″ · OH, etc., where R″=Ca. These are termed "hydrobasic groups" and according to the number of R″-atoms are indicated by (1), (2), etc. By separation of the elements of water in two neighbouring, i.e. ortho-hydrobasic, side-chains, the anhydrobasic groups:

$$\begin{matrix}—O \cdot R'' \\ —O \cdot R''\end{matrix}\Big\rangle O, \qquad \begin{matrix}—O \cdot R'' \cdot O \cdot R'' \\ —O \cdot R'' \cdot O \cdot R''\end{matrix}\Big\rangle O, \text{ etc.}$$

are formed and are distinguished according to the number of R″-atoms by 2°, 3°, 4°, etc. (p. 166).

The porcelain cement powders differ from the above silicate cements inasmuch as they contain only a few silicate side-chains; and the number of R″-atoms is 1.

The following are typical porcelain cements:



$R''O \cdot 6\,Al_2O_3 \cdot 6\,SiO_2$

$R''O \cdot 6\,Al_2O_3 \cdot 5\,SiO_2$

$2\,R''O \cdot 3\,Al_2O_3 \cdot 10\,SiO_2$

etc.

$4\,R''O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

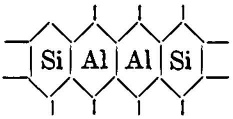
These porcelain cements also differ from other silicate cements in that they only form transparent, stone-like masses when mixed with certain acids, viz. aluminophosphoric acids, or such of their salts as have a certain composition, to be mentioned later.

* The authors of the present volume use the term *acido-* or *baso-phile* (from *philos* =fond of) for any substance which has an attraction for an acid or basic dye-stuff.—A. B. S.

The Attraction of the Aluminosilicates for Acids and Bases

The acido- and baso-philism of the aluminosilicates must be specially considered, as this property of the aluminosilicates plays an important part in the reactions under consideration.

For example, in the hydro-aluminosilicate

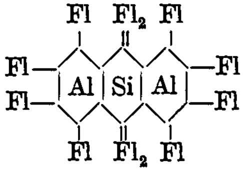


$\overset{\circ}{H}_{12}$ ($\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}$),

both the *a*- and *s*-hydroxyls are acido- and baso-philic, i.e. the *a*-hydrogen and the *s*-hydrogen may be substituted by monovalent acid and basic radicles. There is a great difference between the degree of acido- and baso-philism * of these hydrogen atoms: the *a*-hydrogen atoms are strongly acidophilic and only feebly basophilic, but the *s*-hydrogen atoms are strongly basophilic and are only feebly acidophilic.

These properties of hydro-aluminosilicates, which are very important in connection with the reactions which occur in the hardening of cements, may be further shown in the following:

1. The topaz molecule



must, if the foregoing hypothesis is correct, have the monovalent fluoric acid radicle strongly bound to the aluminium radicle and only feebly to the weakly acidophilic silicon radicle. In any case the fluorine must be bound more strongly to the aluminium radicle than to the silicon radicle.

The fact that the topazes contain at least 8 fluorine atoms, shows that when natural changes occur the fluorine splits off from the silicon ring and not from the aluminium one, i.e. the fluorine is bound more strongly to the aluminium than to the silicon ring, as the theory implies.

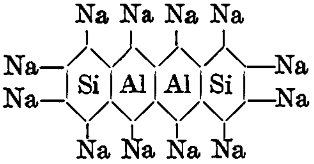
2. The relatively feeble basophilism of the *a*-hydroxyls and the strong basophilism of the *s*-hydroxyls are shown by the interesting studies of Gans[367] on the "artificial zeolites" or "permutites." Gans found that the aluminosilicates showed a variation in the strength of the bond between them and the alkalies and alkaline earths, the bases in some cases being readily and completely replaced by

* See footnote on p. 209.

others, whilst in others, substitution could only be effected with difficulty.

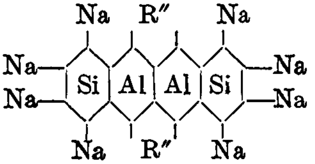
Gans inferred (in agreement with the theory stated above) that the readily replaceable alkalies and alkaline earths are combined with alumina, those bases which are replaced with greater difficulty being attached to the silicon. In other words, he concluded that the *a*-hydroxyls are feebly basophilic and the *s*-OH groups are strongly basophilic.

Gans has applied this ready replaceability of the *a*-bases of the aluminosilicates in an ingenious and practical manner. For instance, in the sodium silicate A, viz.:



A.

the *a*-sodium must be readily replaced on treatment with aqueous solutions of Ca, Fe″, Mn, etc., forming B, viz.:



B.

R″=Ca, Fe, Mn, etc.

Conversely the compound A may readily be formed by treating B with an aqueous solution of sodium chloride.

The great technical importance of such properties of the *a*-bases is obvious. Thus, by suitable treatment of the sodium silicate A with water, it can remove calcium and magnesium bases from solution, i.e. it can be made use of in softening hard water.

The *a*-bases may also be used for other industrial purposes, e.g. to replace potassium in molasses and syrups in the sugar industry by sodium or calcium.

For this reason the following patents (see Siedler[368]) are interesting:

(*a*) An invention for treating water for domestic and technical purposes, distinguished by filtering the water through hydrous aluminosilicates, whereby the undesired bases such as iron oxide, manganese oxide, lime, magnesia, etc., are replaced by others which are desirable or at least harmless.

(*b*) An invention for replacing the potash, in sugar syrups and molasses, by other bases, distinguished by filtering the said syrups and

molasses through aluminosilicates, whereby an exchange of bases occurs, the potassium in the syrups being replaced.

3. The acido- and baso-philism of the aluminosilicates are also shown by their amphichromatophilism, i.e. their relation to both acid and basic dye-stuffs, as has been shown by Hundeshagen[369] in the case of kaolin. Concerning this, Hundeshagen wrote: "A peculiar form of amphichromatophilism is observable in kaolin, which behaves as though the silica and alumina could act independently towards dye-stuffs. The influence of the silica is by far the strongest, and it is to this that clay owes its very basophilic character; almost equal, in fact, to that of amorphous silica. At the same time there is a weaker, yet still distinct, oxyphilism which is completely analogous to the oxyphilism of free alumina."

Hundeshagen therefore considers that in the kaolin molecule there are both alumina-hydroxyls (=*a*-hydroxyls) and silica-hydroxyls (=*s*-hydroxyls).

4. The acido- and baso-philism of kaolin may also be observed in the colours known as "kaolin-lakes," which are formed by the action of kaolin on acid and basic dye-stuffs. The basophilism is stronger than the acidophilism, so the kaolin lakes with basic dye-stuffs play a highly important part in technology of lakes, whilst kaolin-lakes containing acid dye-stuffs have a much feebler colouring power and are, technically, of much less importance.

5. According to Hundeshagen, the acido- and baso-philism of kaolin are due to the fact that kaolin can withdraw acids from acid solutions and bases from alkaline ones.

6. The acidophilism of the *a*-hydroxyls of kaolin is shown by the constitution of ultramarine, and particularly from the behaviour (observed by Silber) of the compound:

$$\overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$$

towards HCl and that of the product thus formed,

$$\overset{\circ}{Na}_{8}\overset{\circ}{H}_{4}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}),$$

towards $AgNO_3$, as well as by the formation of the sodalites (p. 152).

The somewhat strong acidophilism of the *a*-hydroxyls and the very strong basophilism of the *s*-hydroxyls are of importance in connection with physio-chemical reactions which take place during the hardening of the porcelain cements, as described in the next section.

(*c*) The Physio-chemical Reactions occurring during Hardening

The hardening of porcelain cements is physio-chemically analogous to that of other silicate cements, such as Portland and slag cements, the molecules undergoing a series of hydration phases, just as do those of Portland cement (p. 173). The porcelain cements are also "hydraulites" (p. 174), but, unlike the Portland and slag cements, they only harden in the presence of certain acids. If the powdered portion of a

porcelain cement is more basic than usual, acid salt solutions may induce hydration phases.

Two classes of porcelain cements may, conveniently, be distinguished :

1. Porcelain cements of which the fluid portion is acid—acid cements or *A*-cements.

2. Porcelain cements of which the fluid portion is an acid salt solution *—saline or Σ-cements.

The Σ-cements have several advantages over the *A*-cements.

The chemical reactions involved in hardening porcelain cements consist chiefly of two parts :

(*a*) Hydration, and

(*b*) Condensation, or formation of an acid or salt with simultaneous loss of water.

(*a*) Hydration

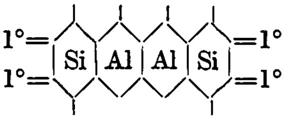
Hydration consists, as in the hardening of Portland cement, in a series of hydration phases as shown in the following example :

$4\,RO \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(a)

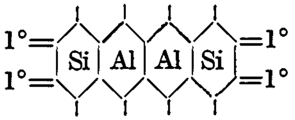
$4\,RO \cdot 2\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(b)



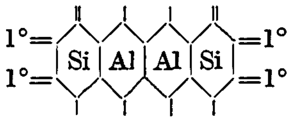
$4\,RO \cdot 3\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(c)



$4\,RO \cdot 4\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(d)

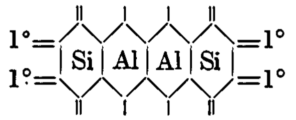


$4\,RO \cdot 5\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(e)

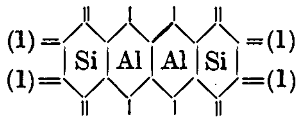
* Although the term "acid salt solutions" is used for convenience, it should be understood that acid-reacting salts are really meant, and not the true acid salts which contain H-ions. Solutions of metallic salts are known (p. 228), which do not appear to contain H-ions and yet have an acid reaction.

Even if the acid reaction of these fluids is referred to the presence of H-ions, or if these ions should be found in some of them, there still remains a large difference between a porcelain cement containing free acid and one containing an acid salt, particularly when the physiological action of the cement is considered.



$4\,RO \cdot 6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(f)



$4\,RO \cdot 10\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$

(g)

This large number of hydration phases is accompanied by a notable development of heat, particularly at the beginning.

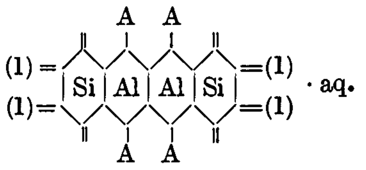
(*b*) Condensation

As soon as the hydration—assisted by the acid or acid salt solution—ceases, the second stage of hardening—condensation—commences.

If the fluid portion of the cement is a complex acid, as shown by the acidophilic α-hydroxyls, water will be separated and the acid radicle will attach itself to the silica molecule.

On account of the somewhat strong acidophilism of the α-hydroxyls on the one hand and the very strong basophilism of the s-hydroxyls on the other, it is highly probable that acids will attach themselves to the silica ring without any separation of base from the silica side of the molecule.

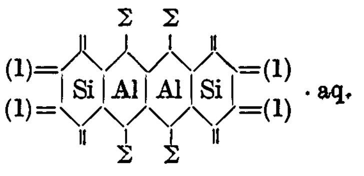
The constitution of a hardened mass of an *A*-cement will, thus, be :



According to this constitution, if, for instance, A is an alumino-phosphoric acid, such a substance must be a strongly acid salt of a triple acid.

The addition of a complex acid to a cement powder is by no means a neutralisation of the former in the ordinary sense of this word, although on account of its insolubility the hardened mass may react neutral to litmus. There is, in fact, a large number of substances which, being insoluble, react neutral to litmus and yet are, constitutionally, acids. Kaolin is a typical substance of this kind.

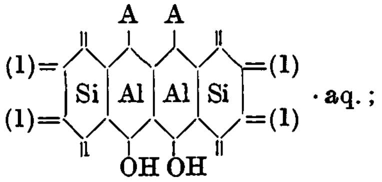
A hardened Σ-cement has probably an analogous constitution :



A completely saturated substance of this kind is, therefore, analogous to Thugutt's sodalites (p. 60) and the Σ-ultramarines whose mode of formation has been shown in previous pages to be due to the formation of condensation products. The *A*-cements, on the contrary, are analogous to the *A*-ultramarines (p. 140).

These structural formulæ indicate that a molecule of a cement may be combined with four molecules of acid or of Σ, but this can only be the case occasionally.

The above structural formulæ for fully saturated dental cements are only for a given case, as the structure of these substances must, naturally, vary with the ratio of powder to fluid. Some of these cements may, for example, have the formula



others contain an excess of acid (Σ) or of uncombined *A* or Σ. The constitution of hardened cements of other compositions may be regarded as analogous.

The physio-chemical reactions occurring during hardening are thus clearly shown by means of this theory. On the physical side, the following may be added :

If the cement mass is regarded as a sphere composed of different layers as in Fig. 3,[370] the hardening takes place from the circumference towards the centre. The outer layer *a* hardens without any external pressure, but in the case of *b*, any expansion is opposed by the hardening outer layer *a*. The same occurs with layers *c* and *d*, only they cannot expand so much. Hence the hardness and density of the mass must increase as the interior is approached and the outermost layer must be the softest. An examination of phosphate cements confirms this view, the outer portion of an old dental stopping being more or less worn, whilst the interior is found to be much harder.

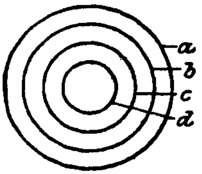


FIG. 3.

Consequences of the Theory and the Facts

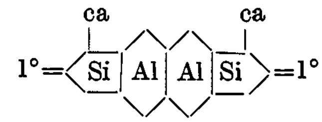
A

From the theory it follows that the formulæ calculated from the analyses of the porcelain cements must be arranged to represent compounds whose existence is theoretically possible. Unfortunately, very few analyses of porcelain cements have been published. The

investigations of the authors[371] have shown that the powders contain approximately

CaO	Al_2O_3	SiO_2
6 – 12%	38 – 50%	40 – 44%

One analysis leads to the formula



(Ca=½ CaO)

	3 CaO	· 6 Al_2O_3	· 10 SiO_2	· Loss on ignition
Calcd.	11.20	40.80	40.60	8.00
Found	12.10	38.19	40.60	8.23

The 6 – 12% CaO in the porcelain cements shows that the powder contains fewer R″ side-chains than the Portland cements. This relatively small proportion of CaO also explains the great resistance of these cements to acids, as experiments with complex acids have shown that the power of the molecule for combining with a base increases inversely as the amount of base present (pp. 94, 108, 262, 263, 265, etc.). The non-separation of this CaO by the action of the fluid portion of the cement may also be regarded as being due, in all probability, to the acidophilism of the Al- and the basophilism of the Si-rings.

B

The absorption of water during hardening must be capable of being represented stoichiometrically, as it is in Portland cements. The hardened mass must contain various forms of combined water : water as —R″ · OH, water in the form of OH-groups attached to the silicon ring and "water of crystallisation." Of these, the maximum amount of water combined with —R″. and with silicon respectively must *a priori* be capable of prediction. No direct determinations of these forms of water have been published.

C

The hydration of the porcelain cements must proceed gradually like that of the Portland cements. It must, therefore, be possible to prove a gradual growth of the various OH-groups by determining the amount of water in the porcelain cements at various periods during the hardening.

This consequence of the theory was confirmed, in the case of Portland cements, by a series of hydration experiments by v. Teicheck and others (p. 180), but no such determinations have, as yet, been made with porcelain cements.

D

The duration of the various hydration phases is a very interesting subject. In the case of the porcelain cement powders, with their relatively low content of base, the duration of the hydration phases must, *cæteris paribus*, depend on the following factors :

1. The constitution of the silicate molecule.
2. The acidity of the cement acid.
3. The temperature at which the hardening occurs.
4. The proportion of water in the cement fluid.
5. The physical conditions of the cement powder.

As regards the first factor—the constitution of the silicate molecule—it is clear that the various silicate molecules must hydrate at different rates.

As an increase in the acidity of the cement fluid must increase the speed of hydration, it is clear that, *cæteris paribus*, those porcelain cements of which the fluids contain more acid must harden more rapidly than those with a less acid fluid.

As, on the contrary, the hydration begins more readily when the basic content of the silicate molecule is increased, a reduction of the acidity of the cement fluid must effect a corresponding increase in the basic content of the silicate molecule if a definite rate of hardening is to be reached.

The temperature at which the hardening occurs exercises an important influence on the rate of hardening, the higher the temperature the quicker the hardening, and *vice versâ*. The extent to which the rate of hardening is increased by a rise of (say) 10° in temperature must be determined by direct experiment.

For a definite acidity in the fluid portion of the cement, the rate of hardening must naturally depend on the proportion of water in the fluid: the larger the proportion of water the more rapid the hardening, and *vice versâ*, as in the former a quicker, and in the latter a slower hydration occurs.

The ability of the silicate molecule to undergo hydration also depends, *cæteris paribus*, on the physical condition of the cement powder : the coarser the powder the slower and feebler the hydration, the finer the texture the greater its reactability.

This consequence of the theory is fully confirmed by experience. With some *A*-cements the hardening is so rapid that the powder must contain coarse grains as well as fine ones in order to reduce the rate of hardening within convenient limits, or special instructions must be issued to users that the fluid must be added in small quantities and very slowly.

There is a possibility, in the case of some of the slower Σ-cements, of so regulating the rate of hardening that at blood heat (37° C.) they harden at a normal rate and can thus be used for dental purposes. This is effected by arranging the size of the grains in the powder and the concentration of the fluid portion of the cement.

At the ordinary temperature, the Σ-cements usually harden more slowly than the *A*-cements, and a number of writers have considered this to be a defect in the Σ-cements. As a result of this slower hardening of the Σ-cements they contain uncombined Σ (i.e. uncombined, feebly acid salts) in solution for a longer time after the commencement of the hardening than do the *A*-cements, and, consequently, they have an acid-like reaction towards litmus for a longer period. This has led to the false conclusion that the Σ-cements are detrimental to the pulpa.

In reaching this conclusion the following have been overlooked :

1. That the dental cements should not harden at the ordinary temperature, but at blood heat, and this is, as already shown, the temperature at which they harden best.

2. No importance can be attached to the suggestion that these cements are harmful to the pulpa, as the reddening of litmus by them is not due to a strong *A*-acid, but to a weakly Σ-acid salt solution.

E

It also follows from the theory, that the hardening of a porcelain cement must occur in a series of phases. This consequence of the theory is fully confirmed by practical experience. Morgenstern[372] has shown that, in most cements, the first hardening is followed by molecular changes, which in some cases are completed within 3 hours, but in others are not fully completed in 24 hours. In confirmation of this is the fact, proved by Morgenstern, that the strength of these cements increases if, after the first period of 3 to 24 hours, they are kept out of contact with air or moisture.

Wege[373] has also distinguished two stages in the hardening of porcelain cements.

1. The setting stage, which, according to Wege, "lasts 15 to 20 minutes. If it takes place at blood heat, it is accompanied by a marked evolution of heat owing to the rapidity with which the physiochemical changes occur. During this stage these cements become so hard that they may be cut and polished. At ordinary room temperature the hardening takes place much more slowly.

"The sensitiveness of the freshly mixed cement to moisture and to saliva is characteristic of the first stage of the hardening of a porcelain cement. It is, therefore, necessary to perform the operation of tooth-stopping in such a manner that all saliva is excluded until the cement is hardened."

2. The stone-forming stage commences "after 15 to 30 minutes (at blood heat). The chemico-physical reactions which occur during this second stage of the hardening are less energetic than those in the first stage, and the heat evolved is so small as to be scarcely measurable."

"The mass in the second stage is less sensitive to moisture and saliva. This sensitiveness—which shows itself by 'killing' any cement

mass mixed with saliva—diminishes more and more until it eventually ceases completely.

"The 'stone-forming' process may be completed in a few hours or it may take 2 to 3 days, different cements varying considerably. It is during this second stage that the cement attains its maximum hardness and density."

Schreiber[374], in his critical studies, has also repeatedly called attention to the various phases of hardening of the porcelain cements.

The inference from the theory that the hardening of the porcelain cements occurs in a series of phases is thus in agreement with the facts.

It is clear that, previous to the "stone-forming" stage, the hardening of the porcelain cements may be hindered by the action of water, alkalies, and diluted acids, and it is a serious error, in studying the resistance of these cements to acids and alkalies, to treat them with these reagents before the stone-forming stage of the hardening is completed. As already mentioned, Morgenstern and Schreiber have clearly shown the nature of this error in a series of experimental studies made by them.

F

In the light of the H.P. theory, the fact that porcelain cement masses have a higher resistance to dilute acids than is possessed by ivory or the enamel of natural teeth is explicable. The acid in the fluid portion of the cement does not decompose the silicate molecule; it does not cause the separation of any bases which can form easily soluble salts with phosphoric acid or aluminophosphoric acid. The acid in these cements only assists the hydration of the silicate molecule and adds itself to the latter. Dilute acid, if it does not act on the hardened molecule, may, if it has as great an affinity for the silicate molecule as the cement acid, effect a further hydration and may replace it, though this is seldom the case, with dilute lactic and acetic acids.

This indicates that the cement mass is not readily attacked by acids, a fact which has been proved experimentally.

The Toxic Action of the *A*-cements in the Light of the New Theory

From what has been written in the foregoing pages, the constitution and properties of the porcelain cements must, undoubtedly, be regarded as new members of the great class of silicate compounds. It is therefore desirable, in the light of the H.P. theory, to find an answer to a question which is both theoretically and practically of the greatest importance. It has been stated that some porcelain cements have a serious disadvantage in that they cause dangerous inflammation and destroy the nerves (pulpa) of the teeth, with all the consequences which follow these actions.

For several years there has been a bitter fight as to whether the toxic character of these silicates may be prevented. The chief difficulty in solving this problem appears to lie in the lack of knowledge of their

constitution and the course of the reactions during the hardening of the material. Moreover, the question as to the toxic action of porcelain cements containing strong acids (the *A*-cements are the only ones which have been found to affect the pulpa) is purely a physiologico-chemical one, and yet no one has endeavoured to answer it with the assistance of physiological chemists and their discoveries of toxines, although this would seem to be a *conditio sine qua non* to any satisfactory solution.

The following lines contain the results of an effort to ascertain the cause of the harmful action of some cements and to find a means of preventing it. This effort is based on a consideration of the constitution and the reactions occurring in the hardening of *A*-cements and on a study of the manner in which the toxines have been found to react physiologically.

In studying the causes of the toxic action of the *A*-cements the following consequences of the theory are important:

1. The action of the acids in the fluid portion of the *A*-cements—the alumino-phosphoric acids—results, primarily, in the hydration of the silicate molecule, i.e. in the formation of acid and basic hydroxyls. The combination of the acid with the molecule is a secondary result, and is due to the acidophile OH groups.

The cement, prepared by mixing the powder and the fluid together into a plastic mass, is at once forced into the dental cavity under considerable pressure. It is, therefore, clear that it must contain a considerable amount of free alumino-phosphoric acid which may gradually find its way to the pulpa.

2. According to the theory, which is based on the fact of the strong basophilism of the silicate ring and the weak acidophilism of the alumina ring, it follows that, in all probability, the free alumino-phosphoric acid will not cause the separation of the least particle of base. This highly probable consequence of the theory becomes a certainty when the repeatedly observed high resistance to acids of the uncombined or incompletely combined *A*-cements is taken into consideration.

This consequence of the theory, which is in complete agreement with the observed properties of the cement masses, is of great importance in studying the causes of the toxic action of the *A*-cements. Thus, it might be assumed that the 6–12% lime in the *A*-cement powders would be separated on mixing the powder with the acid fluid, and that if the lime present reached a definite proportion it might, in this way, completely prevent the toxic action of the acid owing to the combination of the acid and lime. From both the theory and the observed behaviour of the *A*-cements towards acids it follows that no such separation of the base can occur.

The improbability of any separation of lime being brought about by the alumino-phosphoric acid on simply mixing the silicate powder and the acid fluid together, is confirmed by the behaviour of highly

basic cements which have been hardened by treatment with acid, such as the zinc phosphate cements, the powdered portion of which contains 90% of zinc oxide.

In commerce, as may readily be seen from a study of the literature of the subject, there are two kinds of zinc phosphate cements :

(*a*) Those in which the fluid portion contains a strong, free acid ; and

(*b*) Those in which the fluid portion contains a considerable amount of a stronger base, e.g. zinc oxide.

The difference is shown in the following Table, due to H. Paschkis :

Composition of Zinc Cements

Name	" Fluid Portion "	Contains
Poulson	fluid	no zinc
Entrop	"	" "
Ash	"	" "
Grünbaum	"	little zinc
Poulson	crystalline	much zinc
Rostaing	fluid	" "

It is clear that these two kinds of zinc phosphate cement may have different chemico-physiological properties. In this connection it is interesting to notice that one of the most famous workers—Miller, Professor of Dentistry at Berlin University[376]—comments on the repeatedly observed destruction of pulpæ by zinc phosphate cements (p. 232), whilst another equally famous operator—Prof. Black[377]—has observed no such destruction by zinc phosphate cements. These contradictory opinions can only be explained by assuming that Miller used cements containing free acid, whilst Black used those in which the fluid portion contained salts. Other operators have also reported contradictory results, some recommending the use of a protective medium below the cement stopping and others advising the direct use of zinc phosphate cement as providing the most suitable protection for the pulpa.[378]

The destructive action, on the nerves, of zinc phosphate cements containing strong acids in a free state in the fluid portion can only be explained by supposing that not merely the 6–12% of base in porcelain cements, but even the 90% of base in the zinc cement powder, cannot prevent the destructive action of the free acid on the nerves at the moment when the mass is introduced into the cavity in the tooth.

This surprising fact admits of a complete explanation : the hardening of a cement is essentially a slow physio-chemical process and it cannot, by the time the mass is introduced into the cavity, have proceeded far enough for the neutralisation of the strong acid to effect the separation of the base. This behaviour of the highly basic zinc

phosphate cements thus affords a further confirmation of the improbability of any separation of the base by the action of the cement acids on silicate powders so poor in basic material as are the *A*-cements at the moment of their introduction into the dental cavity.

3. In the light of the H.P. theory, the fully hardened *A*-cements are really "sodalites" (p. 214). The acid is added to the silicate molecule because of the acidophilism of the *a*-hydroxyls. Experience has shown that this acidophilism of the silicate molecule is never strong, and in the case of acid dye-stuffs the "lakes" produced are, technically, of minor importance.

There is a danger on account of the low acidophilism of the *a*-hydroxyls, that after a long time a separation of free acid may occur and the pulpa be destroyed, the *A*-cements thus resembling a sleeping volcano which may start its destructive action at any moment.

According to the new theory, the completion of the hardening of the *A*-cements need not prevent the acid in them from acting detrimentally. Definite reports made by various practical dentists show that the deleterious action has been observed a long time after the "stopping" had been inserted; in some instances after an interval of a whole year. In one case, disease of the pulpa, resulting in the death of the patient, set in more than a year after a shallow cavity had been stopped with *A*-cement.

The toxic action of the *A*-cements has now been shown to be due to that of the free aluminophosphoric acid present. The question arises as to whether this toxic action can be proved by chemico-physiological experiments in which these free acids are compared with other toxic substances. The answer to this question forms the subject of the following section:

The Causes of the Neurotropism of Aluminophosphoric Acids (Ehrlich's Theory)

The term "neurotropism" was suggested by Ehrlich[379] to indicate the poisonous action of any material on nerve-substance.

Before it can be stated that a given substance is, theoretically, a neurotrope it is necessary to understand why modern physiological chemists consider that neurotropism is the result of chemical action. The famous physiologist and bacteriologist, P. Ehrlich, was the first to suggest that only those chemical substances are neurotropic which form a definite chemical compound with the nerve-fibres[380] (side-chain theory). Erhlich reached this conclusion as a result of his study of the so-called vital colour processes. Ehrlich has shown that the various dye-stuffs become localised in the organism according to their chemical constitution. For instance, methylene blue has a special attraction for living nerve-fibres; other dye-stuffs are chiefly retained by the fatty organs and still others by the substance forming the kidneys.

As the theory of the chemical combination of the toxines is of fundamental importance if a satisfactory theory which will explain the

observed properties of porcelain cements is to be obtained, it is necessary to mention briefly those facts having any bearing on the theory which have been observed by all well-known physiological chemists.

Ehrlich's theory is confirmed by the following facts :

1. Analysis of cases of poisoning by toxines. It is well known, for instance, that when toxines are introduced directly into the blood-stream they rapidly disappear.[381] The rapid combination of injected toxines with the blood has also been observed by von Behring[382], A. Knorr[383], Bomstein[384], de Croly[385] and others.

2. The investigations of von Behring[386] on tetanus afford a special confirmation of the theory of the chemical combination of the toxines. If animals which are peculiarly liable to tetanus are inoculated with tetanus poison, this is found in all the organs except the central nervous system. In other words, the poison is only feebly combined in the organs first mentioned, but it enters into definite chemical combination with the nerve-substance and cannot then be detected.

The following fact also supports Erhlich's theory : Knorr has drawn up a "Scale of Sensitiveness to Tetanus," and finds that the poisonous dose for a hen is 200,000 times that for a horse, the amount being calculated in grammes of poison per gramme of animal weight. Hens have been found by Kitasato to be practically immune from tetanus.

The very slight sensitiveness of hens as compared with horses may be explained by Ehrlich's theory as due to lack of combining power. This is confirmed by the experiments of Metschnikoff[387], Azakawa[388], and of Fermi and Pernossi[389], which show that insensitiveness to certain poisons is accompanied by the easy recognisability of the toxine in the organism for a long time after its introduction.

4. The well-known experiment of Robert Koch[390] is a particularly valuable confirmation of the theory of the chemical combination of the toxines. Koch wished to sterilise infected animals with corrosive sublimate, but found that the largest practicable doses had no influence on the parasites, the animals being killed more easily than the parasites. This can be readily understood in the light of Ehrlich's theory ; the sublimate is organotropic, but not parasitotropic, i.e. it forms definite chemical compounds with the substances forming the important organs of the infected animals, but has no chemical action on the cells of the parasites.

5. Löw's experiments on the action of oxalic acid on plants, is another interesting and valuable confirmation of Ehrlich's theory.

Oxalic acid is well known as a powerful poison to both animals and plants, and its action was found by Löw to be due to its forming definite compounds with lime salts. Hence, according to Löw, oxalic acid is only poisonous to those plants whose cells contain lime salts, and it can have no poisonous action on plants, the cells of which are free from calcium compounds. Löw has fully proved by direct experi-

ments that plants which contain no lime salts are not poisoned by oxalic acid.

Further important confirmation may be found in the results of a large number of experiments, all of which are fully indicative of the production of definite chemical compounds.[191]

Amongst others, Pasteur's Immunisation Therapy, Behring's Serum Therapy (Diphtheria serum), Chemo-therapy, the work of Koch and Uhlenhut on the use of atoxyl in the cure of malaria, and the chemical treatment of infectious diseases (syphilis) by Ehrlich and Hata all yield therapeutic results in support of Ehrlich's side-chain theory.

There can, therefore, be no doubt that the theory of the chemical combination of the toxines is fully established.

If it is desired to explain the neurotropism of the A-cements (i.e. the poisonous action of the aluminophosphoric acids on nerve-substance) it must be clearly shown that these substances form definite chemical compounds with the nerve-fibres.

In order to do this it is clearly necessary to:

1. Have a clear idea of the chemical constitution of the nerve-fibres, and
2. Produce facts which show the existence of a chemical relationship between the aluminophosphoric acids and the nerve-fibres.

I. The Chemical Constitution of the Nerve-fibres

The nerve-fibres, like all other animal fibres such as wool and silk, belong to the proteins,[192] i.e. to those substances whose constitutions have been so admirably studied by Emil Fischer and his students. These investigators[193] claim that it has been positively proved that the proteins contain amino-acids, the same fundamental substances appearing in the most widely differing proteins, but in very varying proportions, so that one or other amino-acid may be entirely wanting. This constitution of the proteins is reminiscent of the aluminosilicates which also contain a few fundamental substances combined in the most varied proportions. For instance, in the proteins, the following amino-acids are found: glycocol, *d*-alanine, *l*-leucine, *d*-glutaminic acid, amino-oxysuccinic acid, diaminoacetic acid, etc.

As the complete hydrolysis of proteins by acids and alkalies always yields the same results, E. Fischer and his associates concluded that the amino-acids in them are not secondary, but are an integral part of the protein molecules. Hence the proteins are complex acids and must behave towards acids and bases in a manner analogous to other complex acids. As a matter of fact, the albumens are usually represented as multiple acid bases and multiple basic acids, i.e. they have a marked baso- and acidophilism and form compounds with both acids and bases. This ability of the albumens to combine with acids and bases has been investigated by several methods.[194]

II. The Chemical Relationship between the Nerve-fibres and the Aluminophosphoric Acids

If it may be accepted as a definite fact that the nerve-fibres, like animal fibres generally, are chiefly proteïns (amino-acids), it is clear that such substances may form definite compounds with either simple or complex acids, especially as Friedheim and his associates have found, as the result of a large number of experiments, that complex acids can not only combine with bases, but also with other acids, and other chemists have proved the existence of amino groups.

That the facts fully confirm the possibility suggested by theory is shown by the mordanting of animal fibres by sesquioxide compounds such as aluminosulphates (alums), aluminoacetates, etc., i.e. by the various complex alumino-acids.[395] The properties of the aluminophosphates—such as the existence of aluminophosphates with very different proportions of phosphoric acid and alumina, which can pass into one another ; the impossibility of replacing the alumina by other bases by double decomposition ; the masking of the phosphoric acid by alumina in agriculture, etc.—show that their constitution is analogous to that of the aluminophosphates and aluminoacetates, and there can be no doubt that they have a special chemical relationship to the nerve-fibres. In short, the aluminophosphoric acids are, in accordance with Ehrlich's theory, neurotropes or nerve poisons.

It is very probable that the proteïns, like the aluminosilicates, have a cyclic constitution, i.e. they apparently consist of N- and C-hexites and pentites. The combination of animal (nerve) fibres and the complex alumino-acids—the corrosives—is most probably analogous to that of the complex acids : two neighbouring OH-groups in the animal fibre combining with two similar (ortho) OH-groups in the alumino-acid with loss of water. The resultant complex can then, in an analogous manner (i.e. on losing water), unite with dye-stuffs, the combination of these being thus effected by means of the OH-groups in the alumino-acids. From this it follows that only dye-stuffs with ortho-hydroxyl groups can combine with alumino-acids and can be used as dyes. This interesting consequence of the theory has been fully confirmed by the experiments of C. Liebermann and St. Konstanecki[396], who have shown that the only oxyanthracinones which are fixed dyes are those containing two ortho-hydroxyl groups. C. Liebermann has converted non-dyeing colours into strong dyes by the introduction of two ortho-hydroxyl groups, particularly in the case of fluorescines, eosines,[397] malachite green,[398] fluorines,[399] oxyaurenes,[400] etc.

What can be said in regard to the physiologico-chemical action of the Σ-cements ?

The experience of Black and Schreiber with Σ-phosphate cements shows that the Σ-silica cements are non-poisonous to the nerves of the teeth. The plastic mass of Σ-cement does not contain free alumino-

phosphoric acid, but an acid saturated with zinc oxide, i.e. a zinc salt, which must, naturally, behave in a different physiologico-chemical manner towards the nerves. According to Ehrlich's theory, all toxic action is excluded in the case of Σ-cements, as investigations on the dyeing of animal fibres show[401] that, in the absence of mordants, the colour can only be fixed on wool and silk when the dye-bath is acid, i.e. only when the dyestuff-acid is in a free state. From this it follows that only free acids have any action on the nerve-fibres, salts being inert in this respect; in other words, solutions of zinc salts can form no definite chemical compound with nerve-fibres, i.e. they are not neurotropic.

It is very remarkable that, according to Siem's investigations,[738] complex compounds of aluminium (sodium alumino-lactate), when injected subcutaneously into animals, are found to be *highly poisonous*. On injecting relatively large doses of these compounds into the blood, death occurred after seven to ten days. The daily subcutaneous injection of small quantities into dogs, cats and rabbits, caused death within three to four weeks after the introduction of a total weight of 0.25 to 0.30 grammes Al_2O_3 per kilog. of animal weight.

The fact discovered by Döllken[739] in repeating Siem's experiments is even more interesting. Döllken confirmed Siem's conclusions and also found that, in accordance with the H.P. theory, these poisonous aluminium compounds are *essentially nerve poisons*. He found that in animals which had died from injections of these substances the nerve-roots were degenerated and that marked changes had occurred in the nerve-cells. The central nervous system is the part most affected by these poisonous aluminium compounds; the outlying nerves not being appreciably affected.

Siem and Döllken have also shown that it is a further characteristic of aluminium poisoning that time is required before any symptoms of poisoning are observable. Neither investigator noticed any acute symptoms of poisoning, even when large doses were administered. This experience is a complete agreement with the symptoms accompanying poisoning by silicate cements of the "A" type, in which, as previously stated, the action of poison does not make itself observable until after weeks, months, or, in some cases, more than a year.

The objection may be raised that, according to the H.P. theory, neutral salts of complex alumino-acids and particularly sodium alumino-lactate, should be *non*-poisonous, as the harmlessness of the zinc aluminophosphates (i.e. of the Σ-cements) was thus explained. This objection is not well taken, as it is necessary to remember that some salts, like the sodium compounds of complex acids, readily dissociate and their *anions* can then enter into reaction. For this reason the feebly dissociable zinc salt possesses advantages over the free acids. Moreover, it is especially important to observe that Siem used extremely dilute solutions, whilst the fluid portion of the Σ-cements is highly viscous and is thus different from the *A*-cements. The prob-

ability of extensive dissociation or decomposition of the fluid portion of the Σ-cements in hollow teeth is very remote.

It should also be noted that, apart from any particular theory, there can be no doubt that free acids can combine with nerve-substance far more readily than can salts, and from this point of view the Σ-cements must be more advantageous than the *A*-cements for physiologico-chemical purposes.

The objection may be raised that the fluid portion of the Σ-porcelain cements is very concentrated, and that the acid reaction is due to a hydrolysis of the salt, i.e. that these salts must contain free aluminophosphoric acid, even if only in small quantity. This objection is quite erroneous, as the acid reaction of metallic salts is not necessarily a sign of hydrolysis, because many metallic salts (including nickel sulphate, manganese chloride and copper sulphate) which, in aqueous solution, react strongly acid may be shown, on physio-chemical grounds, to be quite free from hydrolysis.

As the question whether the acid reaction of an aqueous solution is a definite sign of the presence of free acid has not been clearly answered, an attempt is made, in the following lines, to deal with it in accordance with the experimental material available.

Does the Acid Reaction of an Aqueous Solution of an Acid Salt always indicate Hydrolysis and the Presence of Free Acid?

The non-hydrolysis of a number of acid-reacting solutions of metallic salts may be shown:

(*a*) By determining their coefficient of conductivity, and
(*b*) By spectrum analysis of the solution.

(*a*) Conductivity Determinations

The following simple means of determining whether a salt is hydrolysed in aqueous solution is due to Ostwald. If the molecular conductivity of a solution of one gramme-molecule of a salt in 1024 litres of water at 25° C. is represented by μ_{1024} and the conductivity of the same weight of the salt in 32 litres of water at the same temperature is represented by μ_{32}, from the difference Δ between these two numbers it can at once be seen whether the substance is hydrolysed or not. If, for instance, the difference Δ is approximately 20, no hydrolysis has occurred, but if Δ is considerably above 20, a hydrolysed salt is present.[402]

A number of salts, such as nickel sulphate, cobalt chloride, manganese chloride, copper chloride and copper nitrate, when in aqueous solutions react like acids, yet the value of Δ shows that according to Ostwald's rule they are not hydrolysed, as may be seen from the following Table,[403] in which no number is significantly above 20.

Conductivity Difference

Salt	Δ
Nickel sulphate	18.6
Manganese chloride	18.5
Cobalt chloride	18.2
Copper chloride	20.5
Copper nitrate	18.6

Copper sulphate also has an acid reaction, yet the determination of the conductivity of a number of aqueous solutions of copper sulphate show, according to Ostwald[404], that this substance is not hydrolysed. Ostwald has shown that the conductivity increases steadily with the dilution of the solution, and from this and from the conductivity of an infinitely dilute solution he concludes that solutions of copper sulphate contain Cu- and SO_4- ions, but no H- ions.

(*b*) Spectrum Analysis

According to Knoblauch[405] and Nernst[406], spectrum analysis affords a very delicate method for showing the constancy, or otherwise, of the constitution of a substance. If the absorption spectrum of a solution of the substance changes with the concentration a change must have occurred in the constitution of the substance. According to Nernst[407], innumerable tests have shown that a very small change in the constitution is readily shown by the difference in the absorption spectrum.

If acid-reacting solutions of metallic salts, such as copper sulphate, underwent the slightest hydrolysis this could be detected by the change in the absorption spectrum, so that by examining the spectrum of solutions of different strengths it is possible to ascertain whether the slightest hydrolysis has taken place.

Acid-reacting copper sulphate which, according to its conductivity, is not hydrolysed in aqueous solution, has also been spectroscopically examined by several investigators, including P. Glan[408], H. W. Vogel[409], and Knoblauch[410]. Glan and Vogel found that the solid and dissolved substances both have the same absorption spectrum, so that no change in its constitution and therefore no hydrolysis occurs when acid-reacting copper sulphate is dissolved in water.

Knoblauch dissolved half a gramme-molecule of copper sulphate in 0.37 litres of water and an equal quantity in 325 litres of water; the character of the spectrum of both these solutions was identical and Knoblauch therefore concluded that in neither case did water effect any hydrolysis of the salt.

In these ways, the best methods of physical chemistry have shown that a number of acid-reacting metallic salts are not hydrolysed when in aqueous solution, i.e. they do not contain any free acid.

The objection may be raised that (*a*) Carrara and Vespignani in measuring the rate of saponification of methyl acetate at 25° C. by

means of copper sulphate, and (*b*) Davis and Fowler by inverting sugar with copper sulphate solution,[411] have shown quantitatively that the hydrolysis of the copper sulphate does occur and that the investigations of these scientists, at first sight, appear to show a slight though definite hydrolysis. These experiments must, nevertheless, be regarded as useless, as Donnan[412], who first introduced them, found that they were by no means free from objection inasmuch as they contradict the results of conductivity determinations. They are specially erroneous as their authors worked on the false assumption that the saponification or inversion was effected exclusively by hydrogen-ions. If this assumption were correct it must follow that :

1. The inversion of the sugar must increase with the dilution of the acid, as the number of the H-ions increases as the solution becomes more dilute. Precisely the opposite is the case: the inversion proceeding more rapidly with the stronger acid.[413]

2. The rate of inversion must be reduced by adding neutral salts of the acid used, as this would reduce the number of H-ions. Yet according to Nernst the opposite is the case: the presence of an equivalent amount of potassium salt of the given acid increasing the rate of inversion by about 10 per cent.

3. Salts which react acid to indicators must also invert sugar, as they should (on the assumption named) contain H-ions. Yet H. Ley[414] has observed that many salts which react acid to indicators behave like neutral salts as regards sugar.

4. Salts which contain no H-ions should never invert sugar, yet H. Ley and others[415] have found that many so-called neutral salts, e.g. chlorides of strong bases, invert sugar to a small yet measurable extent. The contradiction between practice and the theory that H-ions are necessary for the inversion of sugar was explained long ago, Arrhenius[416] having shown that other ions greatly increase the action of the H-ions. If, however, the inversion of sugar may be effected or increased by other ions it is clearly useless to employ this method to ascertain what hydrolysis (if any) has taken place in a given solution. The above-mentioned facts are also opposed to the assumption that sugar inversion can only occur in the presence of H-ions, as Ley and others have effected it in complete absence of these ions. If, on the other hand, it is agreed that anions may influence the inversion, it is impossible to understand why the inversion cannot be due to the SO'_4 ion in the copper sulphate, as two absolutely unexceptionable methods —electrical conductivity and spectrum analysis—have shown the non-hydrolysis of the solution.

There can be no doubt that there are some metallic salts which react like acids and yet do not contain a trace of free acid. Hence the acid reaction of the Σ-cement fluids cannot be used as an argument for the presence in them of free acid ; in other words, the acid reaction of the Σ-cement fluids does not in any way imply the possibility of a chemical combination of the cement fluid and the nerve-fibres.

The physiologico-chemical properties of the *A*- and Σ-cements fully agree with the properties which have been observed in practice.

Practical Experiences with *A*- and Σ-cements in regard to their Physiologico-chemical Behaviour

The numerous experiments already referred to leave but little doubt that the *A*-cements are nerve-poisons and that the Σ-cements are harmless.

In the year 1904 or 1905, shortly after the silicate cements had been placed on the market, several attempts were made to prevent the poisonous action of the *A*-cements. For this purpose Selowsky[417], Hentze[418], Sachs[419], Bruck[420], Detzner[421], Scheuer[422], Escher[423] and others recommended that :

1. A very thick cement mixture should be used so that any excess of poisonous acid in the fluid would eventually combine with the excess of powder.
2. Before inserting the cement, a neutral material should be introduced into the dental cavity, so as to prevent the acid from reaching the pulpa.

In spite of the most careful use of these protective materials, dental literature contains many reports of destroyed pulpæ and of some deaths due to the acid. Thus, in 1906 the following (German) dentists reported cases of poisoning and the uselessness of a stiff paste and of protecting pieces : Heinsheimer[424], Silbermann[425], Reissner[426], and in 1908, Schreiber[427]. In 1909 Baldus[428] confirmed this view. Of the many (German) dentists who in 1909 reported deaths due to pulpa poisoning caused by *A*-cements, only the following need be mentioned : C. Wolff, Aachen[429], Marx[430], Horstmann[431], Schulte[432], Gerhardt, Leipzig[433], Wild[434], Albrecht[435], Peckert[436], Stein-Mannheim[437], Gunzert[438] and Port[439].

Of these, Wild alone found 30 deaths due to *A*-cements. Still more recently, Feiler[440] has reported that in spite of the greatest care, 11 cases of poisoning occurred, and enquired whether it was right to use silicate cements of so dangerous a nature to patients. " I must say that to me each case is a peculiarly unpleasant memory, so that I am constantly asking myself whether we are justified in using a material which, in spite of the greatest care and skill, places the patient in so much danger."

Feiler has also reported a fatal case following the use of an *A*-cement as follows : " The following incident, told to me by Privy Councillor Partsch, is worth careful consideration. I take the following from the official medical report : ' On the 16th December, 1906, a year after the stopping of a superficial cavity in the right upper incisor with original Ascher's silicate cement, R. G. (22 years of age) began to suffer indefinable pains in the right side of his face, and several days later a pronounced swelling of the right cheek and of the upper and lower

eyelids was observed ; fever also commenced. On the 20th December an elastic swelling, very sensitive to the touch, was easily observable ; the teeth were very painful when pressed, and a similar swelling near the *fossa cannia* was seen. The temperature rose to 40° C. with the pulse at 120. General condition much disturbed ; no mental symptoms. The dentist trepanned two, whereupon pus discharged from the *pulum cavum*, the swelling increased around the roots of the teeth and contained an evil-smelling pus. In the evening the temperature was still 38.5°C.; the pain somewhat reduced. Next day, a general improvement. On the 23rd and 24th no pain experienced ; patient taken in closed carriage to the dentist for further treatment. On the 25th he made a long journey unknown to the doctor. On the 26th headache recommenced and on the 27th the doctor was sent for and found considerable feverishness and headache, but no trouble with the mouth, apart from three vomitings. The doctor diagnosed influenza, but the symptoms increased daily, the lid of the right eye swelled, the eyeball was protruded ; general mental symptoms observable ; the pulse sank to 56 and became irregular, the knee reflexion was unsatisfactory, and considerable deep hyperæsthesia of the legs was found.

" On the 4th of January an operation showed that the processes had extended through the *fissura orbitalis inferior* to the eye-socket, and notwithstanding a wider opening it was impossible to prevent the spread of the processes. The temperature fell for a short time, but on the 7th of January it rose to 40.4° C., with feverish shivering, and remained fairly constant with increasing brain disturbance until the *exitus letalis* on the 18th of January."

Schreiber[441] in 1910, after reporting a whole series of fresh deaths from diseased pulpæ due to the use of *A*-cements, wrote in strong terms condemning the impracticability of the preventive methods recommended.

Freund[442], of Breslau, encouraged the use of *A*-cements, and attributed the toxic action of some specimens to the presence of arsenic and not to the free acid. A year later (in 1909),[443] after some unfortunate experiences with *A*-cements, he openly joined those who accept the acid theory and discussed the question as to who were responsible for these " accidents "—the manufacturers who guaranteed their products to be harmless, or the dentist.

Lartschneider[444] distinguishes between an irritation of the pulpa and destroying it. Under the term " pulpa irritation " he groups all the cases in which pain is felt soon after the insertion of the cement. In most cases the pain soon ceased, but in some instances it continued for several hours. He has observed these symptoms in 6 to 8 per cent. of his patients. They were often quite independent of the depth of the cavity, and many of the worst cases were those where no trouble was anticipated. He noticed that young, delicate, anæmic patients suffered most, and considered that the fatal cases might be due to anæmia.

Robert Richter[445] also attributes the harm done by these cements to the presence of arsenic, and points out the seriously poisonous nature of this material. He goes so far as to suggest that the *A*-cements should always be labelled as "poison."

Schreiber[446] also regarded the *A*-cements as poisonous, and urged that they should be scheduled accordingly. He also suggested that in the case of an "accident" the dentist should be held to be legally responsible.

It is interesting to observe that most investigators consider that the poisonous action is due to the free acid.

A. Masur[447] reports observations made by the Breslau dentists on the destruction of the pulpa a short time after the use of *A*-cements, the patients suffering from acute periodontitis. Masur also considers that the cause of the symptoms observed is to be found in the cement acid. Reissner[448] also attributes the periostitis observed by him to the action of free acid.

Silbermann[449] definitely assumes that the detrimental action of the *A*-cements on the pulpa is due to the acid they contain, and has endeavoured to prove this assumption experimentally. Later, he considered that the arsenic in the cements was the cause of their toxic action, but "the difference observed in the pulpa after the application of arsenic and of an Ascher's stopping, which had resulted in periodontitis," led him to conclude that the damage was done by the acid in the cement and not by the arsenic. Moreover, arsenic-free *A*-cements have the same toxic action as others ; hence it is not generally agreed that the acid is the poisonous ingredient.

Kulka[450] has pointed out that, according to Miller[451], the destruction of the pulpa (p. 221) is by no means unusual with zinc phosphate cements, and is apparently due to the phosphoric acid in the cement fluid. Kulka accepts this suggestion and also the similar one made by Ottolenguis[453] ; he also considers it possible that the free acid removes lime from the tooth-ivory and affects the pulpa by partial destruction of the dentine.

Feiler[454] does not accept this view, as he found that on drilling through the stopping the dentine above the pulpa was unaffected, and that no lime had been removed from it ; he does, however, agree that the detrimental action of the *A*-cements is due to the free acid present, and refers to Pawel's[455] work in support of this. Pawel found, by actual experiments on animals, that the acid in these cements can penetrate thick layers of dentine and can then damage the pulpa. According to Feiler, the chemical irritation of the excess of acid affects the vitality of the pulpa through pores or channels in the dentine and destroys its power of resistance to bacteria. The latter are thus able to pass through the channels in the dentine and to enter the bloodstream, thus bringing about violent processes, the intensity of which depends on the virulence or pathogenity of the germs present.

The destruction of the pulpa which results from the use of porcelain

cements containing free acids is attributed to the strong acids in the cement fluid by the following (additional) authorities: Biel[456], Hentze[457], Sachs[458], Bruck[459], Apfelstädt[460], Schreiber[461], Wege[462], Schachtel[463], etc.

Lartschneider[464] has expressed a doubt as to the action of free acid in *A*-cements on the pulpa. He placed small pellets of cotton-wool saturated with the fluid portion of these cements (i.e. with cement-acid) in the cavities in infected teeth and closed the cavity with a Fletcher's cap. In some instances temporary pain was experienced by the patient, but it ceased after a few hours. In no case did he find any appreciable destruction of the pulpa or any periostitic symptoms, even though some of these "acid fillings" were retained in the teeth for nine weeks.

This investigation is of value, but it does not invalidate the "acid theory" for the following reasons:

1. Symptoms are, in many cases, only observed after a very long time, sometimes as much as a year or more after the introduction of the stopping, and the observations made by Lartschneider were made in too short a time for the action of the acid to become noticeable. In this connection the experience of another dentist—Albrecht[465]—is interesting. Albrecht was one of the first to use *A*-cements extensively, and he could not understand why so many of his colleagues complained of their deleterious action. More recently, however, he has realised that several "accidents" are due to old cases, the damage to the pulpa taking some months before it became noticeable. Two cases in particular, in which he filled quite shallow cavities with *A*-cements, resulted in the destruction of the pulpa and in periodontitis after more than a year, have made him pessimistic with regard to these cements.

The eventual destruction of the pulpa in the cases quoted by Lartschneider is, therefore, by no means excluded.

2. The plastic silicate mass is pressed into the dental cavity under considerable pressure, whereby the free acid may the more readily penetrate the pores or channels in the dentine and so reach the pulpa. If a pellet of cotton-wool saturated with acid is used, there is little or no pressure exerted, and the acid cannot so readily reach the pulpa: it may, in fact, combine with the Fletcher cement.

3. It is not impossible that only certain people are sensitive to the action of the aluminophosphoric acids, and that in his experiments Lartschneider had patients who were not likely to develop pulpitis.

If the harmlessness of the aluminophosphoric acids is assumed, to what is the destruction of the pulpa due? Moreover, Pawel has shown the harmful action of strong acids on the pulpa by direct experiments on animals as previously noted (p. 232).

The most direct proof that the toxic action of the *A*-cements is solely due to the free acid they contain is found in the Σ-cements, which only differ from the former in the substitution of a salt for the

free acid, yet are found in practice as well as in theory to be perfectly harmless.

No sooner had the poisonous nature of the *A*-cements been realised than an urgent demand was made for their improvement in such a manner that they should lose their toxic action completely. Thus Heinsheimer[466] has stated that " Beautiful and valuable though the Ascher cements are, they have one property which is absolutely necessary to remove, viz. the toxic action on the pulpa. Otherwise, these almost ideal materials must be discarded. These views are held by a number of my colleagues, and I may frankly say that this serious disadvantage is not due to the use of too soft a mixture or to badly prepared material."

Greve expresses himself to the same effect : " Some of the new silicate cements produce excellent results under suitable conditions, but an improvement is essential. If this cannot be effected they will never attain the popularity which has been prophesied."

The warnings of Heinsheimer, Greve and others are all the more significant when it is remembered that, according to Pfaff[467], diseases of the pulpa are the cause of other diseases of important organs—particularly of the eyes and ears. Thus, deposits of decomposed matter on the pulpa, diseases of the pulpa itself and of the membranes surrounding the fangs, frequently cause neuralgia of the *trigeminus*, or neuritis ascending to the *ganglion gasseri* (Karewski). The clinical observation that the eyes are affected in many diseases of the teeth has been made by numerous ophthalmologists. Acute pulpitis, periostitis and empyemia of the *antrum highmori* are stated to be the causes of many eye complaints by Alexander, Keyser, Wacher, Lardin, Birch-Hirschfeld and others. Pagenstecher and Vossius have also reported numerous cases. Amongst other diseases of the eyes which have their origin in defective teeth are changes in the optic nerves and in the retina ; inflammation of the cornea and of the conjunctiva, or of the whole eye-ball ; diminished sensitiveness in the apparatus for accommodation and in the *iris*, affections of the muscles which move the eye-ball and eyelids, diseases of the tear-glands and ducts. These have been observed by Decaisne, Blank, Schmidt, Schulek, Wedl and others. The manner in which these diseases are brought about must be sought in the nerves and in the mucous lining of the mouth ; the latter extends to the jaw from the *ostium pharyngeum tubæ* to the drum of the ear, so that inflammatory processes in the mouth may also extend their action for a considerable distance. *Otitis media* and the related ascending neuralgia may also be due to diseases of the teeth, according to Böke, Ziem and Winkler.

Greve[468], in 1906, attributed the poisonous nature of the *A*-cements to their irrational composition. He considered that the composition of the silicate powder does not permit it to neutralise the cement acid, and he attributed the dangerous irritation of the pulpa to an excess of free acid. It has been shown that in the highly basic zinc phosphate

cements (p. 221) the use of less acid will not avoid the danger, because no separation of the base has occurred by the time the plastic mass is placed in the cavity. Nevertheless, Greve's work is important because he showed the value of bases for reducing the poisonous nature of *A*-cements. The right way to destroy the poisonous nature of the silicate cements is shown, both by theory and practical experience, to consist in saturating the cement acid with a strong basis before the fluid portion of the cement is mixed with the powder ; in other words, by the conversion of *A*-cements into Σ-cements.

W. and D. Asch[469], in 1908, published the results of some experiments with a transparent Σ-cement, i.e. with a silicate cement in which the fluid portion consists of an acid-reacting salt solution. Use of this cement in practical dentistry appears to be highly satisfactory : the mass proved, in accordance with theory, to be perfectly harmless to the pulpa. The practical experiences of Oppler[470], Wege[471], Schachtel[472], Schreiber[473], Baldus[474], etc., with this cement have further confirmed its absolute harmlessness.

Baldus has used this cement for more than a year, Wege and Schreiber for several years. Schachtel has laid this cement on almost translucent pulpæ, which were very painful at the time of the operation, but after a long time no harmful symptoms could be observed. Oppler has brought this cement into direct contact with the free pulpa, yet though the patients were under observation for a long time, he observed no irritating symptoms, a result which, according to Schreiber, is incredible if *A*-cements are used.

Hence, practical experience is in full accord with theory in regard to the absolute harmlessness of the Σ-cements, just as both are agreed as to the essential poisonous nature of the *A*-cements.

The Σ-cements have, in their physiologico-chemical relations, other advantages over the *A*-cements. It is open to argument whether an excess of cement fluid diffuses more rapidly through the dental capillaries and into the pulpa more rapidly when it is in the form of a solution of a salt or an acid. The facts established by Graham[740] afford valuable evidence in this connection. According to Graham, the acids and acid salts diffuse more rapidly from a mixture of basic, neutral and acid fluids than do the basic and neutral ones. The fluid portions of the *A*-cements—which are usually free, or practically free aluminophosphoric acids—diffuse, *cæteris paribus*, more rapidly than the Σ-cements, as the latter are usually saturated with bases. Should an excess of the fluid portion of the Σ-cements eventually diffuse towards the pulpa, it is by no means improbable that during this time it would come into contact with cement powder and so would become fully neutralised. In this way the slow diffusibility of fluid portions of the Σ-cements is a great advantage, for physiologico-chemical purposes, over the more readily diffusible portion of the *A*-cements.

When it is remembered that in the commercial Σ-cements the fluid is highly viscous, whilst in the *A*-cements the fluid is very mobile, it is

clear that, *cœteris paribus*, the Σ-cement fluid must diffuse more slowly than that of the *A*-cements, and therefore the former cements are preferable to the latter.

XV

A New Theory of Glasses, Glazes,* and Porcelains

A definite part of the silicates known as glasses, glazes and porcelains are, without doubt, definite chemical compounds in the structure of which hexites and pentites play an important part.

Some of the "glasses" are compounds of simple acids, others, like most glazes and the porcelains, are, in so far as they are single chemical compounds, complex acids or the corresponding salts. Dumas[475] considered that glass has as definite a composition as certain minerals or that it is a mixture of certain silicates; the glasses he examined corresponded to the formula $Na_2O \cdot CaO \cdot 4SiO_2$, but, as Berthier[476] has shown, a higher silica content in the glass makes it harder and less fusible, whilst lime increases its resistance to chemical influences; Benrath[477] regards as "glasses" those silicates which correspond to the general formula $RO \cdot 2\,SiO_2$. It is important to observe that it was Benrath who showed that the most suitable composition for all useful glasses (excluding optical ones) lies within the limits of $Na_2O \cdot CaO \cdot 6\,SiO_2$ and $5\,Na_2O \cdot 7\,CaO \cdot 36\,SiO_2$, in which Na may be replaced by K and Ca by Pb. The occurrence of the figure 6 and its multiples is highly significant.

Zulkowski[741] has studied the relationship between the chemical composition and the physical properties of glass, and, for certain specimens prepared by him, he suggests the following empirical formula:

$$M'_2O \cdot M''O \cdot 6\,SiO_2,$$

and the following structural formula:

$$M''\begin{cases} O \cdot SiO \cdot SiO \cdot O \cdot SiO \cdot OM' \\ O \cdot SiO \cdot SiO \cdot O \cdot SiO \cdot OM' \end{cases}$$

In this manner Zulkowski regards glasses as definite chemical compounds. At the same time, he regards the refining stage in the manufacture of glass as a chemical process and not, as is customary, as a purely physical one in which the dross particles are separated on account of their higher specific gravity.

That the $6\,SiO_2$ in the above formula plays an important part in glasses is recognised by Zulkowski, and based on the investigations of Schwarz, which showed that the resistance of glasses to the action

* Glazes are carefully prepared mixtures of minerals which are applied to articles in order to impart a glossy surface or glaze, the covering material being melted into a kind of glass by heating the article in a kiln or suitable oven. Opaque glazes are termed *enamels*, but both words are used somewhat loosely.

of 10 per cent. hydrochloric acid reaches a satisfactory value with glasses of the character examined by Zulkowski. The investigations of Stas and others have also shown that glasses only become resistant to the action of water when their composition is in accordance with the above formula.

It is also of interest to observe that Zulkowski has studied glasses with $5\,SiO_2$ in the molecule—to which he attributes an analogous formula.

In reality, it is not the number 6, but a multiple of this number which is essential, and glasses containing $36\,SiO_2$ are particularly important. Thus, the normal composition of glass is stated by Fischer[742] to be :

$$5\,Na_2O \cdot 7\,CaO \cdot 36\,SiO_2,$$
$$5\,K_2O \cdot 7\,CaO \cdot 36\,SiO_2,$$
$$5\,K_2O \cdot 7\,PbO \cdot 36\,SiO_2.$$

Normal glasses of the following formulæ have also been reported :[743]

$$6\,K_2O \cdot 2\,PbO \cdot 2\,ZnO \cdot 2\,BaO \cdot 36\,SiO_2,$$
$$3\,Na_2O \cdot 3\,K_2O \cdot 3\,PbO \cdot 3\,CaO \cdot 36\,SiO_2,$$
$$3\,Na_2O \cdot 3\,K_2O \cdot 6\,PbO \cdot 36\,SiO_2.$$

It cannot be said that the three latter formulæ represent the minimum molecular weights, as formulæ can be constructed from the same data with less than $36\,SiO_2$. Yet if the above formulæ are regarded as representing the minimum molecular weights, then glasses must clearly have at least 36 molecules of SiO_2 in each glass molecule.

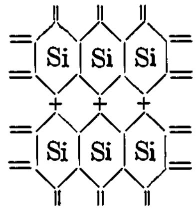
There are many people who believe that glasses are not single chemical compounds, but mixtures or solid solutions. Zulkowski holds the opposite view, and has drawn attention to the experiments of Mylius and Foerster[744], which show that glasses are not mixtures, but true chemical compounds. Zulkowski regards glasses as acid disilicates, because he is not in a position to give a formula similar to those suggested by the H.P. theory.

Of special interest is the composition of *alabaster-glass*, which, according to Zulkowski, is not a double silicate, but a pure potassium meta-silicate which belongs to the siliceous glasses. The composition of this glass he represents by K_2O, $8\,SiO_2$. It is highly probable that this glass has a molecular weight at least four times as large as corresponds to the above, i.e. that the true formula contains $32\,SiO_2$.

In addition to those glasses which may, possibly, be regarded as simple silicates, there are the glazes and porcelains which may be regarded as fused aluminosilicates or salts of other complex silicates, such as salts of borosilicic acid. Zulkowski also considers that "on fusing $4\,SiO_2$, $2\,B_2O_3$ with one molecule of $CaCO_3$ and one molecule of soda, the product is not a glassy mixture, but a homogeneous glass." He attributes to the material obtained in this manner a structural formula analogous to that which he assigns to normal glass.

Assuming that the minimum weight of the chemical compounds

known as " glass " corresponds to a formula with 36 SiO_2 and that this substance is an acid with the constitution



$14\ H_2O \cdot 36\ SiO_2$,

in which the positions marked with a + are either direct bonds between the Si-hexites or are those to which dibasic or sesquioxide-forming elements may be attached, by means of this constitutional formula many hitherto puzzling properties of the " glasses " may be explained.

It should be observed that in this formula the maximum of OH-groups is shown. A series of acids with fewer OH-groups is theoretically possible ; from these a series of salts can be produced as in the case of the complex acids.

The following lines deal with some properties of " glasses " which are explicable by means of this theory :

1. Schott[478] has examined " best Thuringian glass " with a composition corresponding to

	$8\ Na_2O$	$\cdot\ K_2O$	$\cdot\ 4\ CaO$	$\cdot\ Al_2O_3$	$\cdot\ 36\ SiO_2$	
Calcd.	16.05	3.04	7.25	3.30	70.36	
Found	16.01	3.38	7.24.	3.00	69.02	(0.42 Fe_2O_3 and 0.26 MgO)

in a threefold manner, viz :

(*a*) After two years' exposure to air,
(*b*) After heating to 100° C., and
(*c*) After heating to the softening point.

The glasses were carefully cleaned with water, alcohol and ether, dried by prolonged standing over sulphuric acid, weighed before and after treatment with water and finally after heating in an air bath at 150° C. The loss of weight was calculated to milligrammes per sq. cm.

Experiment I : Loss of weight in water 3·5 mg.
" " at 150° C. 0·8 mg.

After heating in water the glass appeared to be unchanged, but after heating in an air bath the whole surface became covered with very fine cracks, but no flakes were split off.

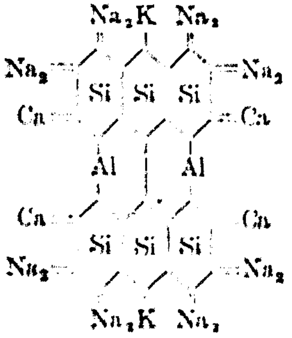
Experiment II : Loss of weight in water 2·5 mg.
" " at 150° C. 0·8 mg.

The cracks produced in the air bath were very fine and could scarcely be seen with the naked eye.

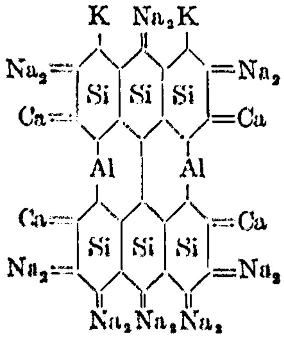
Experiment III : Loss of weight in water 1·8 mg.
" " at 150° C. 0·6 mg.

In this case no cracks could be observed even with a lens.

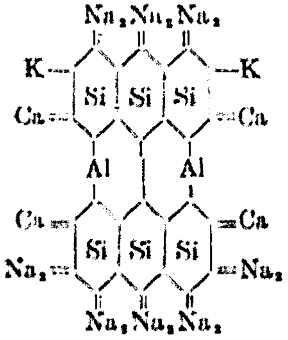
From the results of these experiments it follows that the constitution of the glasses tested must differ, and it should be specially noted that heating this glass to its softening point had notably improved its quality, as is shown by Experiment III. If it is assumed that the dibasic elements and the sesquioxide are strongly bound, but that the alkali-atoms are labile, the following isomers of the original formula may be conceived; these appear to confirm the three foregoing experiments :



A.



B.



C.

It is very probable that, in Experiment III, the compound A is formed, as this has a symmetrical distribution of the atoms in the molecule which would account for its greater stability than the compounds B and C.

It is here assumed that on storing or heating the glasses examined, only the alkali-atoms change places, the dibasic and Al-atoms not being affected. This assumption is justified by the fact, proved by Weber, that very little depression* is shown by thermometer glasses which contain potassium, but no sodium. If this depression is due to a

* When some kinds of glass are used in the manufacture of thermometers, these instruments are found, in course of time, to indicate lower temperatures than they should do. This is referred to as the "depression" of the thermometer; it is commonly understood to be due, in some way, to the chemical composition of the glass employed.

rearrangement of the alkali-atoms within the molecule, those glasses which contain sodium, but no potassium, should show no depression at all. Experiments made by Schott[480] show that this is actually the case.

Thus, glass which contains unmixed alkali (i.e. a pure potash-lime glass) when used for thermometers shows a much smaller error owing to changes in volume than a glass containing mixed alkalies (i.e. containing both potash and soda). Thus, a glass which contains unmixed alkali[745] showed, after a given time, a depression of only 0·04, whilst a glass containing mixed alkali had a tenfold depression, viz. 0.40.

It is a well-known fact that thermometers made of glass containing both potash and soda are erroneous on account of this depression, whilst those made of potash alone are quite satisfactory; this was first pointed out by Weber in a lecture before the Prussian Academy of Science, in December, 1883.

2. It is a well-known fact that the behaviour of various kinds of glass under the heat of a glass-blower's lamp varies greatly: one kind of glass (window glass) turns matt and rough shortly after it has become hot, whilst the glass made in the Thuringian Forest can withstand repeated heating and cooling, and may be blown into various shapes and re-melted without showing any signs of physical change.

Schott's[481] experiments on Thuringian glass have shown that it has the following composition:

	$8.25\ Na_2O$ ·	$1.25\ K_2O$ ·	$0.25\ MgO$ ·	$4.25\ CaO$ ·	Al_2O_3 ·	$36\ SiO_2$
Calcd.	16.21	3.72	0.37	7.54	3.23	68.93
Found	16.01	3.38	0.27	7.38	3.38	67.74

An analysis of the sand used in its manufacture showed:

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
91.38	3.66	0.47	0.31	Trace	2.99	0.50

Schott therefore assumed that this glass owes its valuable properties to the alumina it contains, this being derived from the sand. He has confirmed this by preparing various glasses synthetically from pure quartz to which various quantities of alumina were added, and found that the latter enabled the glass to be worked satisfactorily in the blower's lamp, whilst the former left much to be desired. The value of alumina has also been confirmed on the large scale; the addition of felspar or alumina to a glass mixture invariably improved the working qualities of the glass.

Seger[746], also, made exact experiments on the action of alumina in glass mixtures, and has shown that it increases the fusibility of the mixture and that the tendency to devitrify is reduced. Weber, in an exhaustive treatise on "Depression Phenomena in Thermometers," has stated that alumina is highly important in the manufacture of glass: it increases the fusibility and makes it easier to work.

Schott has also repeatedly observed that the tendency to crystallise or devitrify, shown by many glasses with a high percentage of alkaline

earths, may be diminished by the addition of alumina. This peculiar property of small amounts of alumina (2% to 3%) is readily understood in the light of the H.P. theory of the constitution of glasses; it is due to the bonding of the silicon hexites by the Al-atoms. Definite complexes are formed and may be conveniently termed γ-complexes.

The presence of very small proportions of one substance in another has frequently a very marked effect on the latter. Thus, Marignac[484] has shown the enormous influence of 2 per cent. of silica in silicotungstates; W. Asche[485] and Parmentier have shown the equal importance of 2 per cent. of silica in the silico-molybdates, and it is very probable that the small amounts of Ce_2O_3 in the rare-earths used for gas-mantles,[486] phosphoric acid in the blood, and carbon, tungsten and other "impurities" in steel play a highly important part in the characteristics of these substances.

3. Förster[482] and Kohlrausch[483] have independently proved experimentally that glass is attacked by pure water more strongly than by acids. Förster has also found that a given glass will lose the same weight when treated with sulphuric, hydrochloric, nitric or acetic acid, of either one-thousandth of the normal,* or ten times the normal strength. With concentrated acids, Förster found the action to be weaker t an with more dilute ones.

This property may be explained in the light of the H.P. theory, as follows: The water causes *primary* alkali to become separated from the molecule, and this, to some extent, reacts in a *secondary* manner on the hexite and partially converts it into pentite, as the authors of the present volume have frequently observed in studying the complex salts. With acids, on the contrary, only the acid-water reacts and causes a partial separation of the alkali in the glass. This alkali is at once neutralised by the acid and so is prevented from having any secondary action. In this manner the more powerful action of water, as compared with acids, may be explained.

4. The cause of the phenomenon known as "devitrification" was, until quite recently, extremely puzzling and has not been ascertained with certainty. For instance, Zulkowski considered that devitrification is due to the presence of subsidiary silicates. Thus, a glass made from a mixture corresponding to the formula:

$$9\,Na_2O + 10\,CaO + 60\,SiO_2,$$

is stated by Zulkowski to be:

$$\underbrace{8\,(CaO \cdot Na_2O \cdot 6\,SiO_2)}_{\text{True glass.}} + \underbrace{2\,(CaO \cdot 4\,SiO_2) + Na_2O \cdot 4\,SiO_2}_{\text{Subsidiary silicates.}}$$

The glass is thus regarded by Zulkowski as composed of 8 molecules of normal glass with 2 molecules of calcium tetra-silicate and 1 mole-

* "Normal acid" is of such a strength that 1 c.c. of it will exactly neutralise 0·040 gramme of NaOH or 0·053 gramme of Na_2CO_3, hence 1 c.c. of "one-thousandth normal" or milli-normal acid will exactly neutralise 0·000040 gramme NaOH and 1 c.c. of "ten times normal" acid will neutralise 0·400 gramme NaOH or the equivalent weight of any other alkali.

cule of sodium tetra-silicate. These subsidiary silicates are, according to Zulkowski, the cause of devitrification.

In the opinion of the authors of the H.P. theory, the experiments of M. Gröger[748] throw a special light on the subject of devitrification and lead to the true causes of this phenomenon. Gröger examined a devitrified bottle glass made in the works of the Austrian Glasshüttengesellschaft at Aüssig. It consisted of crystalline nodules which, on fracture, were composed of radial fibres of a matt greenish-white tint. In these nodules completely transparent, dark green masses are embedded. Gröger analysed both the transparent masses and the less transparent devitrified portions and found that their chemical composition was identical and corresponded to the general formula :

$$2.5\ R_2O \cdot 4.5\ RO \cdot Al_2O_3 \cdot 15\ SiO_2,$$

	$0.25\ K_2O$	$2.25\ Na_2O$	$0.25\ MgO$	$3.5\ CaO$	$0.5\ MnO$	$0.25\ FeO$	Al_2O_3	$15\ SiO_2$
Theory:	1.64	9.75	0.70	13.70	2.48	1.24	7.13	63.36
Found in devitrified portion:	1.52	9.76	0.61	13.38	2.49	1.39	7.73	63.79
Found in transparent portion:	1.45	9.78	0.73	12.81	2.47	1.39	7.42	64.39

In this manner Gröger confirmed the statement of Pelouze that the devitrified portions are of the same composition as the glass itself, and also that of Benrath in which the errors in the view previously held, that a devitrified glass is more siliceous than a normal glass, were exploded.

Gröger also investigated the physical and chemical properties of both portions in order to ascertain the cause of the devitrification. He showed that the two portions differed considerably in both physical and chemical properties. For instance, the transparent portion is much more fusible than the devitrified portion.

Again, when treated with concentrated hydrochloric acid the devitrified portion was almost dissolved completely, whilst the transparent portion remained unattacked. From this, Gröger concluded that the devitrified portion consisted of two different substances and endeavoured to separate them by digesting for twelve hours with concentrated hydrochloric acid. Both portions—the soluble and the insoluble—were analysed and conformed to the following formulæ :

For the soluble portion :

$$10.25\ RO \cdot 0.75\ R_2O \cdot 0.12\ SiO_2.$$

For the insoluble portion :

$$1.75\ RO \cdot 2.25\ R_2O \cdot Al_2O_3 \cdot 12\ SiO_2.$$

These figures were deduced from the following data :

	$0.25\ FeO$	$9.5\ CaO$	$0.5\ MgO$	$0.75\ Na_2O$	$12\ SiO_2$		
Theory	1.35	39.80	1.49	3.48	53.88		
Found	1.16	39.30	1.33	3.57	52.89	0.27 MnO	0.36 K_2O

	0.25 FeO	0.25 MnO	CaO	0.25 MgO	2 Na_2O	0.25 K_2O	Al_2O_3	12 SiO_2
Theory	1.67	1.65	5.20	0.92	11.53	2.18	9.48	67.37
Found	1.88	2.60	5.83	0.73	11.27	1.28	9.44	66.97

In the light of the H.P. theory, the devitrification of this mass is readily explained. The clear portion consists of a perfectly stable penta-compound which, in time, parts with a simple silicate and is converted into a hexa-compound. Gröger interpreted his results in a similar manner and considers that the devitrification is due to an unmixing of the glassy mass. In other words, devitrification is not a molecular change, such as occurs when amorphous arsenic acid is converted into the crystalline modification (Pelouze), but the conversion of an unstable compound into a stable one by the separation of a definite constituent. This conclusion agrees completely with the interesting results obtained by O. Schott[740] in the microscopical examination of numerous devitrified products. Schott found that devitrified glasses contain crystals of wollastonite (calcium silicate), and the existence of this substance as an integral part of devitrified glass is shown in the above analysis.

. . . .

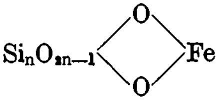
As far back as the year 1900, Zulkowski[741] endeavoured to refer the properties of glass to its chemical constitution and found that, at that time, the only properties to which glass manufacturers and others paid much attention were of an æsthetic nature, such as the shape of the articles made, and the colour, transparency and light refractivity power of the glass. The chemical properties of glass, i.e. its resistance to weather, water and various chemicals, had scarcely been studied at all, and Zulkowski very wisely pointed out that many articles of a domestic or æsthetic nature, to say nothing of the innumerable technical and optical articles made of glass, and those used in the experimental sciences, require that glass should possess not only certain physical properties, but the still more important chemical ones, and yet the study of the latter has been almost entirely neglected.

Nevertheless, the chemical structure attributed to glass by Zulkowski does not sufficiently explain the various properties which have been mentioned in the present chapter, whereas the H.P. theory does explain them satisfactorily.

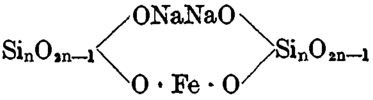
The Chemical Constitution of Coloured Glasses

Coloured glasses of the most varied tints may be prepared by means of suitable preparations of copper, silver, gold and iron, and attempts to learn the chemical constitution of these glasses have been made by numerous chemists. Zulkowski, for instance, regards them as mixtures of various silicates, one of which contains the colouring

oxide. Thus, according to him, the ferrous oxide in a glass is contained in a silicate of the following formula :

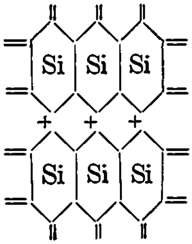


or

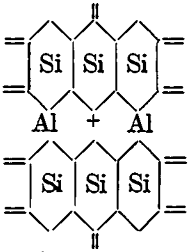


The constitution of coloured glasses is of extreme importance, both scientifically and artistically. The most widely adopted view is that glasses are colloids and that the colouration is of a colloidal nature. That the source of the colour of glasses is analogous to that of organic compounds does not appear to have been suggested, and it is therefore of great interest to consider it with the assistance of the H.P. theory. When this is done the surprising conclusion is reached that coloured glasses possess a structure analogous to that of the organic dye-stuffs and that the colour of the glass is due to the chromophore groups and salt-forming groups in accordance with the theory which Witt devised for organic dye-stuffs.

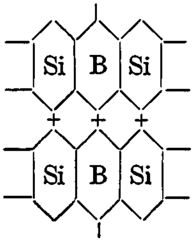
Glasses do not belong to a single class, but, as their analyses indicate, to several classes of compounds, some of which are simple and others highly complex. This may be readily observed in the following types of glasses :



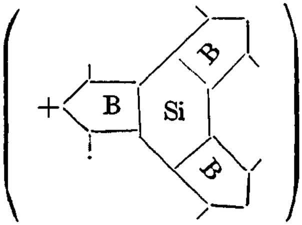
$8\,R_2O \cdot 6\,\dot{R}O \cdot 36\,SiO_2$
A.



$8\,R_2O \cdot 2\,\dot{R}O \cdot Al_2O_3 \cdot 36\,SiO_2$
B.



$4\,R_2O \cdot \dot{R}O \cdot 6\,B_2O_3 \cdot 24\,SiO_2$
C.



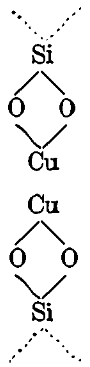
$(3\,R_2O \cdot 7.5\,B_2O_3 \cdot 6\,SiO_2)_2$
D.

etc.

In the positions marked + not only acid groups, but also groups of metallic oxides (in either *-ous* or *-ic* form) may enter. The introduction of such acid or metallic oxide groups may conveniently be termed *central acidising* or *central metallising* and the groups themselves may be termed *centralisers*.

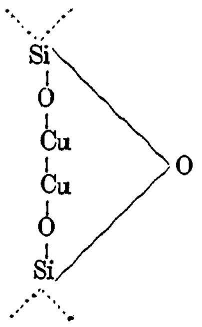
All these centralisers have an important influence on the rings, as will be shown later. At the moment, however, the metallic centralisers are the most interesting, as they give to compounds containing them the property of absorbing certain selected rays of light, i.e. *the metallic centralisers are excellent chromophores.*

The structure of these chromophore groups may be explained as follows: The positions marked + in the foregoing structural formulæ are supposed, for the moment, to be occupied by CuO. One of these positions may then be represented by:



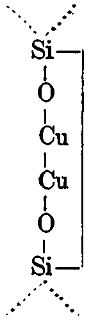
A.

This group may lose oxygen and so be converted into the group:



B.

On further reduction, group B forms the group :



C.

Group C can also part with oxygen or copper.

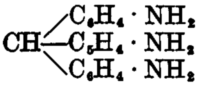
Group B is the chromophore group which, on reduction, forms the leuco-group C. The latter, on oxidation, again forms the chromophore group B. If, during this re-oxidation, a little of the separated metal remains unoxidised, a coloured glass will be obtained in which small quantities of free metal occur simultaneously with the chromophore group.

Decolouration by reduction and re-colouration by oxidation have been repeatedly observed in organic dye-stuffs. It was first pointed out by C. Gräbe and C. Liebermann[750], who found that all the coloured organic compounds which they examined became colourless on reduction. The reduction may cause the direct addition of hydrogen without the loss of any element from the molecule, or it may be effected by the simple removal of oxygen from the compound.

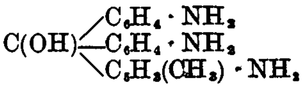
Besides the chromophore groups, the side-chains have also an important influence on the colour. In coloured glasses these side-chains are of a basic nature, and, in accordance with Witt's theory, these glasses should be classified as "basic colours."

Witt's Theory.—According to O. N. Witt[751], the colour of aromatic compounds is due to the simultaneous presence of a colour group or chromophore, and of a salt-forming group. The chromophore is more active, i.e. it produces a stronger colour, when the dye is a salt than when it is in the state of either a free acid or a free base.

In organic dyes and colours, the colour-substances must contain chromophore centralisers such as are required for coloured silicates by the H.P. theory. Such colour-substances are typified by some dyes containing the so-called triphenylmethane group. The oxidation products of the compounds :

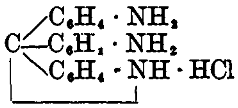


Paraleucaniline.

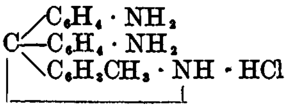


Rosaniline.

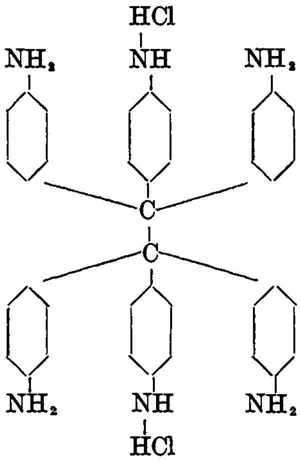
and the substances

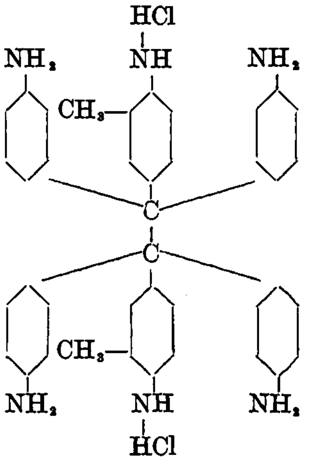


and



are basic dyes on account of the basic groups, though the materials from which they are prepared—paraleucaniline and rosaniline—are colourless. The structure of these colours may, according to the H.P. theory, be written as follows :





These new structural formulæ are in as complete agreement with the properties of these substances as the ones generally seen in text-books and have, in addition, the following advantages :

1. They show a complete analogy with the coloured glasses, inasmuch as both the organic compounds and the glasses are shown to contain chromophore centralisers ; in the former case, carbonic centralisers.

2. As distinct from the usual structural formulæ, the new ones show definite symmetry, which makes the new formulæ more probably correct than the older ones.

3. The difficulties connected with difference in behaviour between the central ring and the two others in the older formulæ do not occur in the new formulæ, as in the latter the groups are arranged differently. There are many other instances in which this difficulty, encountered when the text-book formulæ are used, is avoided by the employment of the new formulæ.

With the assistance of the H.P. theory in combination with that of

Witt, the possible existence of the following coloured glasses containing copper may be predicted :

Type I.

A. $8\ R_2O \cdot 6\ R'O \cdot 3\ Cu_2O \cdot 36\ SiO_2$
B. $8\ R_2O \cdot 10\ R'O \cdot 3\ Cu_2O \cdot 36\ SiO_2$
C. $8\ R_2O \cdot 12\ R'O \cdot 3\ Cu_2O \cdot 36\ SiO_2$
D. $8\ R_2O \cdot 16\ R'O \cdot 3\ Cu_2O \cdot 36\ SiO_2$
E. $8\ R_2O \cdot 17\ R'O \cdot 3\ Cu_2O \cdot 36\ SiO_2$
F. $8\ R_2O \cdot nR'O \cdot 2\ Cu_2O \cdot 36\ SiO_2$
G. $8\ R_2O \cdot nR'O \cdot Cu_2O \cdot 36\ SiO_2$
H. $p(8\ R_2O \cdot nR'O \cdot 36\ SiO_2) + q(8\ R_2O \cdot nR'O \cdot Cu_2O \cdot 36\ SiO_2)$

Type II.

A. $6\ R_2O \cdot 4\ R'O \cdot Cu_2O \cdot B_2O_3 \cdot 36\ SiO_2$
B. $p(6\ R_2O \cdot 4\ R'O \cdot Cu_2O \cdot B_2O_3 \cdot 36\ SiO_2) + q(6\ R_2O \cdot 4\ R'O \cdot B_2O_3 \cdot 36\ SiO_2)$

Type III.

A. $7\ R_2O \cdot 7\ R'O \cdot Cu_2O \cdot Al_2O_3 \cdot 36\ SiO_2 + 7\ R_2O \cdot 7\ R'O \cdot Al_2O_3 \cdot 36\ SiO_2 + Cu_2$
B. $p(7\ R_2O \cdot 7\ R'O \cdot Cu_2O \cdot Al_2O_3 \cdot 36\ SiO_2) + q(7\ R_2O \cdot 7\ R'O \cdot Al_2O_3 \cdot 36\ SiO_2) + rCu_2$, etc. etc.

These three types of glass must obviously differ in their properties. The glasses in the first group are simple silicates, those in the second group are the Gamma Complexes, in which the copper is more strongly combined than in group I. In the third group the glasses are also Gamma Complexes, in which free metallic copper occurs in addition to the copper in combination.

[The existence of coloured glasses containing other metals in place of copper and of a completely analogous constitution is equally possible.]

The H.P. Theory and the Facts

Only one glass in the first group mentioned above has yet been prepared, namely *Porpora,** which, according to Zulkowski[752], corresponds to the formula :

$$8\ R_2O \cdot 17\ R'O \cdot 3\ Cu_2O \cdot 36\ SiO_2.$$

* Porpora glass is defined as a glass which has a rusty red colour by reflected light and a purple-blue colour by transmitted light, the colour being due to a small proportion of copper added to the batch.

The analysis of this glass when re-calculated, in accordance with formulæ suggested by the H.P. theory, is as follows :

	$6.25\ Na_2O$	$1.75\ K_2O$	$4.5\ CaO$	$10.5\ PbO$	$1\ FeO$	$1\ MnO$	$3\ Cu_2O$	$36\ SiO_2$
Theory	6.57	2.79	4.27	39.74	1.22	1.20	7.28	36.91
Found	6.31	2.60	4.31	39.06	1.29	1.50	7.89	35.80

Trace Al_2O_3

Zulkowski has also analysed a glass belonging to the second group and known commercially as *Copper Ruby*. This analysis corresponds to the formula :

$$6\ R_2O \cdot 4\ R'O \cdot 0.5\ Cu_2O \cdot B_2O_3 \cdot 36\ SiO_2$$

	$3.25\ K_2O$	$2.75\ Na_2O$	$0.5\ SnO$	$0.75\ MnO$	$1.75\ PbO$	$1\ CaO$	$0.5\ Cu_2O$	B_2O_3	$36\ SiO_2$
Theory	9.10	5.07	1.99	1.59	11.62	1.67	2.12	2.08	64.76
Found	9.11	5.13	2.16	1.91	10.71	1.52	1.63	2.53	64.80

Traces of $FeO \cdot Al_2O_3 \cdot MgO$

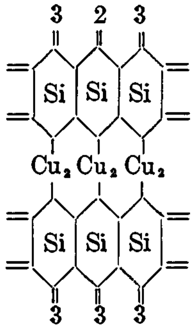
Zulkowski has also analysed *aventurine*, a glass belonging to the third group. Part of the copper in aventurine glass is in the free state, but if all the copper is considered to be in combination the analysis corresponds to the formula :

$$7\ R_2O \cdot 7\ R'O \cdot Cu_2O \cdot Al_2O_3 \cdot 36\ SiO_2$$

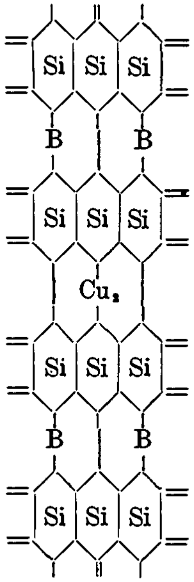
	$1.5\ K_2O$	$5.5\ Na_2O$	$0.5\ PbO$	$0.25\ FeO$	$5\ CaO$	$1.25\ MgO$	Cu_2O	Al_2O_3	$36\ SiO_2$
Theory	4.19	10.15	3.22	0.53	8.33	1.49	4.25	3.03	64.71
Found	4.46	10.22	3.07	0.68	8.74	1.57	4.90	2.16	64.52

The structural formulæ of these glasses when arranged in accordance with the H.P. theory are as follow :

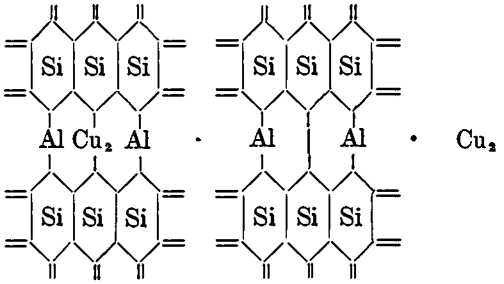
Porpora glass



Copper Ruby glass

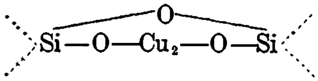


Aventurine glass



A large series of facts which have, hitherto, been inexplicable is in complete agreement with these structural formulæ. For example :

(*a*) On comparing the structure of the ruby glass with that of the porpora, it is clear that the chromophore



in the ruby glass is in the first γ-complex, whilst the corresponding chromophore groups in the porpora glass are combined with a simple polymerised silicate.

From the H.P. theory, a *masking* of the Cu_2O in copper ruby glass may be predicted, i.e. this oxide will not be recognised by ordinary tests so readily as it is in the porpora glass. This interesting consequence of the theory is found to be in complete agreement with the experimental evidence.

According to Rose and Hampe[753], cuprous oxide and silver nitrate react as follows :

$$3\,Cu_2O + 6\,AgNO_3 + 3\,H_2O = 2\,Cu_2H_3NO_6 + 2\,Cu(NO_3)_2 + 6\,Ag.$$

Zulkowski[752] used this reaction in his studies of the copper ruby and porpora glasses and found that whilst the porpora glass effected a separation of metallic silver in accordance with the equation, the copper ruby glass showed no such separation, even after many weeks.

(*b*) From the structural formulæ of these three glasses it follows that only the aventurine contains free metallic copper. The facts fully confirm this consequence of the theory. For example, Wöhler found

that on placing this glass in a solution of mercuric chloride it became white and copper entered into solution—a clear sign of the presence of metallic copper. It might, of course, be argued that cuprous oxide, which is also present in aventurine glass, would produce the same result, but this argument has been met by Zulkowski[752], who treated the powdered glass with an ammoniacal solution of copper. In the presence of metallic copper the reaction with this solution would be

$$Cu + CuO = Cu_2O,$$

and the solution must be decolourised. Zulkowski placed a weighed quantity of finely powdered aventurine glass in a test tube and then added an ammoniacal solution of copper sulphate in such an amount that the metal in it was equal to one-quarter of the copper in the glass. The tube was then sealed and heated on a water bath. After 15 hours the deep blue colour of the solution was entirely discharged, thus proving beyond all doubt that aventurine glass contains free copper.

Zulkowski has also shown by similar tests that porpora and copper red glasses contain no free copper. In the case of porpora the colour of the solution was not affected in the least nor was the tint of the glass changed, even after three years. The test was not so prolonged with the copper red glass, but even after several weeks the colour of the solution was not changed in the least. These tests show beyond all question that the porpora and copper red glasses contain no free metallic copper, but that it is present in aventurine glass. They also shatter the opinion, commonly held, that the colour of the two glasses first named is due to their ability to dissolve metallic copper and retain it in solution in its metallic state.

(*c*) The structural formulæ of porpora, copper red and aventurine glasses also show that the colour is due to a definite chromophore group and not merely to dissolved cuprous oxide as is frequently stated. The investigations made by Seger[754] on coloured cuprous glasses are in full agreement with this consequence. This investigator showed that an alternately reducing and oxidising atmosphere is necessary in the production of these glasses, and that the difficulties in manufacture were not so much due to the glass itself as to the correct atmosphere in the furnace. Seger found that the same glass-mixture would produce all shades, from black, through brown, to bright red or yellowish green, and that different parts in the same melt would vary enormously in colour, according to the nature of the gases which entered the crucible ; that some melts would be of good colour whilst others of the same batch would be quite devoid of red and would, instead, be black or grey.

All these variations show that red glass must have a definite chemical constitution, that it must contain certain chromophore groups, and not be merely a solution of copper or cuprous oxide. Seger confirmed this view when he added 1 per cent. of cupric oxide to a glass corresponding in composition to

$$3\ Na_2O \cdot 3\ CaO \cdot 3\ B_2O_3 \cdot 15\ SiO_2.$$

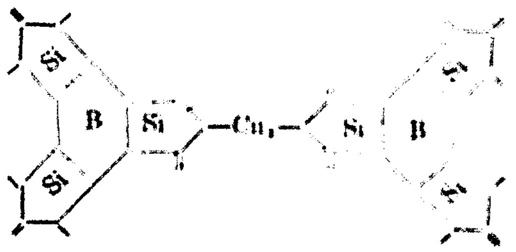
This mixture was placed in a porcelain crucible which was then placed in a platinum one. The platinum crucible was fitted with a porcelain lid through which protruded a porcelain tube of small bore. On heating the crucible to 400° to 500° and passing a stream of hydrogen or carbon monoxide through the tube, the copper oxide was reduced, but the glass did not fuse; it merely formed a red clinker. On raising the temperature to 950° and continuing the stream of reducing gas, the metallic copper previously formed disappeared, the particles dissolving in the molten glass, and the colour of the glass changed from red to a greenish grey. On powdering this grey glass and re-heating with white glass to which a little oxidising agent, such as 1 per cent. iron oxide, tin oxide or a sulphate like gypsum, had been added and substituting a stream of air for the former reducing gas, Seger obtained a red glass.

He explained this phenomenon by supposing that the oxygen converted the black metallic copper * into red cuprous oxide and the latter gave the glass its red colour. Seger suggested the three following equations as showing what occurred with different oxidants:

$$2\,Cu + Fe_2O_3 = Cu_2O + 2\,FeO$$
$$2\,Cu + SnO_2 = Cu_2O + SnO$$
$$2\,Cu + SO_3 = Cu_2O + SO_2.$$

The correctness of the last equation is confirmed by the voluminous development of gas during the fusion.

The red glass thus formed may clearly be represented by the following formula:



in which it is assumed that only a portion of the glass contains the chromophore shown. Otherwise, the proportion of cuprous oxide would have to be higher than that actually present.

The phenomena observed by Seger are in complete conformity with the consequences of the application of the H.P. theory to coloured glasses.

(*d*) It has, hitherto, been impossible to understand why coloured glasses should contain such small quantities of free metallic constituents. Not only can this fact now be explained, but it is a direct consequence of the H.P. theory.

* Strictly, this is not metallic copper at all, but the leuco-compound or the reduced leuco-compound (p. 246).

(*e*) According to the theory there is a definite maximum for the metallic constituents to which the colour of glasses, etc., is due. This maximum is not exceeded in the glasses mentioned on preceding pages, and further investigations will only show that it must not be exceeded.

It is highly probable that glasses containing silver and gold are completely analogous to those containing copper, but to prove this it will be necessary to re-calculate the analyses of these glasses and to consider their characteristics and properties with the aid of the H.P. theory.

In reviewing the German edition of the present work, C. Desch[736] urged that the use of "definite formulæ" for glass and porcelain is unjustifiable. This is not surprising, as Desch has so strongly committed himself to the view that cements, glasses and porcelains are all "solid solutions." Of various theories, that one is most likely to be correct which explains the most facts and permits the prediction of the most properties, and on this basis the H.P. theory, like all others, must be judged. The authors of the H.P. theory have never suggested that the structural formulæ they assign to various substances are in any sense "final," and they readily admit that they must be altered whenever other formulæ which correspond with more properties are discovered. Meanwhile, the fact that, at present, they explain more properties than any other formulæ yet devised is a sufficient reason for the formulæ deduced from the H.P. theory. Moreover, so far as the authors of this theory are aware, there is, at present, no real ground for doubting the correctness of their conclusions. On the other hand, what good does it do to assume that glasses are mixtures or solid solutions? Such a view, which is held by many chemists, including all the chief critics of the H.P. theory, does not in any way advance the cause of science, because it fails to explain more than a very small proportion of the facts, whilst an enormously large number of them are fully explicable in accordance with the H.P. theory. Under these circumstances, is it too much to say that the deductions from the H.P. theory approximate far more closely to the true structure of the substances concerned than do the "mixture" and "solid solution" hypotheses?

It should be observed that in this volume the authors have made no attempt to show that *all* commercial glazes, glasses and porcelains are definite chemical individuals, though, without doubt, many of them are such. In the following pages the analyses of a number of glasses, glazes, and porcelains have been calculated into the molecular form, those materials being selected which, on account of their excellent physical and other properties, appeared likely to consist of definite chemical compounds. This calculation of the formulæ should prove of value in the further study of these materials.

Formulae of Glasses, Glazes, and Porcelains

The following analyses of three Jena glasses are taken from Hovestadt's book on the subject :

(*a*) Jena glass 3 III has the following composition :

$$3\ Na_2O \cdot 3\ CaO \cdot 0.25\ Al_2O_3 \cdot 0.75\ B_2O_3 \cdot 12\ SiO_2$$

Calcd.	16.07	14.52	2.20	4.53	62.67
Found	16	16	2	4	62

(*b*) Jena glass 6 III has the following composition :

$$3\ Na_2O \cdot 0.5\ K_2O \cdot 0.75\ Al_2O_3 \cdot 0.25\ B_2O_3 \cdot 15\ SiO_2$$

Calcd.	15.18	3.84	4.17	2.84	73.97
Found	15	5	5	2	73

(*c*) Jena glass 13 III has the following composition :

$$1.5\ K_2O \cdot 2.5\ ZnO \cdot B_2O_3 \cdot 10\ SiO_2$$

Calcd.	13.86	19.91	6.86	59.37
Found	15	20	7	58

(*d*) The composition of a glass highly prized for champagne bottles, analysed by Maumené[487], is :

$$4\ CaO \cdot 2\ Na_2O \cdot 0.25\ K_2O \cdot 0.25\ Al_2O_3 \cdot 0.75\ Fe_2O_3 \cdot 12\ SiO_2$$

Calcd.	18.05	9.98	1.89	2.05	9.66	58.37
Found	18.60	9.90	1.80	2.10	8.90	58.40

According to F. Fischer[488], the composition of the glaze ordinarily used for porcelain corresponds to the formula :

$$RO \cdot 1\ \text{to}\ 1.25\ Al_2O_3 \cdot 10\ \text{to}\ 12\ SiO_2.$$

The following Tables have been calculated from various analyses of porcelain and porcelain glazes published by Seger[489].

I. Formulae of Porcelain Glazes

No.	Percentage of									Molecules				Sources of glazes
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	H_2O	RO	R_2O_3	RO_2	H_2O	
1.	73.24	—	13.97	0.31	2.57	0.51	4.81	1.71	3,83	2.0	2	18	3.0	Berlin porcelain glaze (old, probably of Dr. Elsner's period).
2.	76.11	—	14.61	0.66	1.44	0.42	2.99	3.03	1.23	1.5	2	18	1.0	Pegmatite glaze from L. Sazerat in Limoges.
3.	74.99	—	14.80	0.37	1.09	0.36	4.31	3.49	0.65	2.0	2	17	0.5	Porcelain glaze from Limoges (per Held & Co., Mayence).
4.	64.96	—	12.74	0.80	8.78	—	1.95	2,30	0.19	3.5	2	17	8.0	Japanese porcelain glaze from Arita. No. 2.
5.	61.97	—	12.92	0.39	9.59	—	4.17	1.12	0.91	3.5	2	16	8.5	Japanese porcelain glaze from Arita, No. 1.
6.	64.88	1.39	14.33	1.39 (FeO)	10.09	1.55	5.61	—	—	4.5	2	15	—	Chinese celadon glaze.

II. Formulæ of Porcelains[490]

No.	Percentage of SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	H_2O	Molecules R_2O	R_2O_3	SiO_2	H_2O	Source of the Porcelains
1.	63.95	25.59	0.69	0.54	2.07	0.98	6.62	0.5	3	12	4.0	Société anonyme de Hal (Belgium).
2.	63.07	24.67	0.59	0.40	4.25 Alk.	—	7.00	0.5	3	12	4.5	Berlin porcelain, 1877
3.	63.48	25.00	0.51	1.06 CaO	2.26	1.19	6.76	0.5	3	12	4.0	A. Hache & Pepin, Schalleur, Vierzon.
4.	60.53	26.37	0.75	0.69 CaO	2.95	1.44	6.39	0.5	3	12	4.0	L. Sazerat, Limoges, body for heavy porcelain.
5.	60.42	26.47	0.52	1.37 CaO	2.75	1.60	7.19	1.0	3	12	5.0	L. Sazaret, Limoges, ordinary body
6.	76.75	18.44	1.17	0.02 CaO	4.23	0.17	—	0.5	3	18	—	Japan IV, Biscuit of egg-shell porcelain.
7.	71.31	19.74	0.73	0.17 CaO	4.04	0.1	4.01	1.0	3	18	3.0	Japanese Body II.
8.	71.60	18.71	1.19	—	4.16	0.18	4.68 & org. Subst.	1.0	3	18	4.0	Japanese Body III.
9.	65.79	23.51	0.31	1.59 CaO	2.01	1.73	5.89	1.0	3	15	4.5	Guerin & Co. (Body for figures).
10.	69.32	23.64	0.83	0.86 CaO	2.66	1.82	5.98	1.0	3	15	4.5	Guerin & Co. (superior body).
11.	65.61	23.07	0.65	0.80 CaO	2.94	2.72	4.50	1.0	3	15	3.5	Guerin & Co., (superior body).
12.	66.00	22.59	0.36	1.68 CaO	2.71	1.80	5.59	1.0	3	15	4.0	Guerin & Co. (ordinary body).
13.	64.52	22.07	0.97	2.10 CaO	1.35	3.13	5.60	1.0	3	15	4.0	J. Poyat, Limoges (ordinary body).
14.	66.78	22.70	0.55	0.97 CaO	1.07	1.51	6.07	0.5	3	15	4.5	Carlsbad Body I.
15.	65.17	23.63	0.51	1.09 CaO	2.92	0.90	5.98	0.5	3	15	4.5	Carlsbad Body II.
16.	64.28	23.49	0.87	1.77 CaO	1.11	3.07	5.48	1.0	3	15	4.0	J. Poyat, Limoges (superior body).
17.	66.97	20.92	0.64	2.06 CaO	2.75	0.41	5.43	1.0	3	16	4.0	A. Hache & Pepin (superior body).
18.	52.94	28.91	0.48	3.99 CaO 0.17 MgO	1.7	0.68 2.48 CO_2	9.12	2.0	6	18	10.0	Sèvres, Body for table-ware.
19.	74.53	16.09	1.03	0.06 CaO 0.25 MgO	4.37	1.19	2.83	1.0	2	15	2.0	Japanese Body I.

From a study of the foregoing formulæ it will be seen that there is a great probability of the hexites or pentites playing an important part in the structure of the substances under consideration.

XVI. The Hexite-Pentite Theory as a General Theory of Chemical Compounds

The following facts make it appear probable that the new hexite-pentite, or more briefly the H.P. theory, which originated in connection with the aluminosilicates, is capable of application as a general theory of chemical compounds.

A. The H.P. Theory and the Composition of the Metal-ammonias and the Related Compounds

The H.P. theory appears to be of special value with regard to the constitution of the metal-ammonias and the related compounds. In Gmelin-Kraut's "Handbuch" (1909. V, p. 337) a number of compounds termed metal-ammonias are described, and from the empirical formulæ there given, the following may be selected as being likely to contain hexite or pentite radicles :

$[Co(NH_3)_6]_2Cl_4(PtCl_6)\ \frac{1}{2}\,H_2O$, $[Co(NH_3)_6]_2(PtCl_6)Cl_6 \cdot 2\,H_2O$,
$[Co(NH_3)_5][Cr(CN)_6]$, $[Co(NH_3)_6][Fe(CN)_6]$, $[Co(NH_3)_6][Co(CN)_6]$,
$[Co(NH_3)_5][Fe(CN)_6] \cdot 1\frac{1}{2}\,H_2O$, $[Co(NH_3)_5][Co(CN)_6]$,
$[Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$, $[Co(NH_3)_4NO_2]SO_4 \cdot H_2O$,
$[Co_2O_2(NH_3)_{10}](NH_3)_4 \cdot 2\,H_2O$, etc.

Of special interest are the compounds :

$$\left[O\begin{matrix}\diagup Co_2NH(NH_3)_8\\ \diagdown Co_2NH(NH_3)_8\end{matrix}\right]X_8,$$

$$X = NO_2,\ Br,\ Cl,\ \text{etc.}$$

$Co_4(NH_3)_{10}(NO_2)_{12} \cdot H_2O$, $Co_4(NH_3)_{10}(NO_2)_{12}$,
$Co_4(NH_3)_{10}(NO_2)_{12} \cdot H_2O$, $Co_2(NH_3)_{10}(SO_4)_2CO_3 \cdot 4\,H_2O$.

Also the compounds :

$2\,Na_2O \cdot Co_2O_3 \cdot 5\,N_2O_3 \cdot H_2O$,
$3\,Na_2O \cdot Co_2O_3 \cdot 6\,N_2O_3 \cdot H_2O$.

and the cobalt oxalates :

$Na_3(NH_4)_3Co_2(C_2O_4)_6 \cdot 7\,H_2O$,
$K_3Na_3Co_2(C_2O_4)_6 \cdot 6\,H_2O$,
$K_6Na_{12}Co_6(C_2O_4)_{24} \cdot 32\,H_2O$, etc.

The hexites clearly play an important part in the following complexes of nitric acid, prepared by Oppenheim[491] :

$K_4Ni(NO_2)_6$, $K_2BaNi(NO_2)_6$, $K_2SrNi(NO_2)_6$, $K_2CaNi(NO_2)_6$,
$K_2PbNi(NO_2)_6$ and $Ba_2Ni(NO_2)_6$,

from which it is impossible to substitute another metal for the Ni by any of the ordinary methods of double decomposition,

The following penta-compounds :

$K_3Cu(NO_2)_5$, $K_3Zn(NO_2)_5 \cdot 6\,H_2O$ and $K_3Hg(NO_2)_5 \cdot H_2O$,

also prepared by Oppenheim, are interesting, inasmuch as they show that three-fifths of the OH-groups in pentanitrites behave differently from the others.

Hexites clearly occur, also, in the following compounds prepared by Soenderop[492] :

$2\,(K_2Co_2Cy_{12})HgJ_2$, $Hg_3Co_2Cy_{12} \cdot K_6Co_2Cy_{12}$, $Hg_3Co_2Cy_{12} \cdot Na_6Co_2Cy_{12}$,
K_3CoCy_6, $Na_3CoCy_6 \cdot 2\,H_2O$, $(NH_4)_6Co_2Cy_{12} \cdot H_2O$,
$(NH_4)_6Co_2Cy_{12} \cdot HgCy_2 \cdot H_2O$.

The hexites also play an important part in the yellow and red ferrocyanides, $K_4Fe(CN_6)$ and $K_3Fe(CN_6)$ and in the double salts $FeCl_3 \cdot 3\,KCl$, $CdCl_2 \cdot 4\,KCl$, etc.

The number of compounds whose composition indicates the possibility of hexites and pentites playing an important part is very large, and all attempts to represent these atomically have hitherto proved unsatisfactory.[493] For some of them, structural formulæ have been devised, as Erlenmeyer's[494] and Friedel's[495] formulæ for the ferrocyanides; Blomstrand's[496] formulæ for ferrocyanides and metal-ammonias; Jörgensen's[497] formulæ for the metal-ammonias and Remsen's[498] for the double salts. Kohlschütter[499] has shown that the defects in all these suggested formulæ are due to their limited applicability; instead of a broad general principle, these formulæ are only related to special compounds, and it is not infrequently found that they do not apply to apparently closely related compounds.

A. Werner[500] was one of the first to call attention to the repeated occurrence of the number 6 in inorganic compounds and to utilise this in the formulation of a theory of molecular compounds in which an attempt was made to construct structural formulæ.

[Werner discovered a remarkable series of optically active compounds of cobalt and chromium, whose activity he traced, in this case, to the hexavalency of the elements in question.

He regarded an element as possessing, in addition to its usual or "principal" valencies, what he designated "auxiliary" valencies, i.e. a kind of fractional valency capable of effecting the union of otherwise independently acting molecules like NH_3 and H_2O. For the present purpose it will be convenient to distinguish between these two types of valency, though the manifestation of the latter is understood by Werner to be independent of units, being variable within wide limits with the nature of the atoms combined and the external physical conditions. Under the influence of both principal and auxiliary valencies, the components of a complex molecular compound arrange themselves into zones around the central element. The first zone comprises a maximum of four or six univalent atoms or groups, this number going by the name of "co-ordination number," and each additional component of the complex is relegated to the second zone, where it takes upon itself certain peculiarities in behaviour, notably that of mobility and consequent tendency to ionisation.

For instance, the structure of the well-known complex $CoCl_2 \cdot 6\,NH_3$ was formerly written

$$Cl \cdot NH_3 \cdot NH_3 \cdot NH_3 \cdot Co \cdot NH_3 \cdot NH_3 \cdot NH_3 \cdot Cl,$$

a representation at once unwieldy and inadequate, though consistent with the then prevalent ideas of valency. Werner, however, regards it as possessing the structure:

$$\left[\begin{matrix} NH_3 & & NH_3 \\ NH_3 & Co & NH_3 \\ NH_3 & & NH_3 \end{matrix}\right] Cl_2$$

in which the ammonia molecules are united with the cobalt atom by auxiliary valencies and comprise a first zone (usually marked by square brackets), whilst the two ionisable chlorine atoms fall into a second. The six constituents of the first zone may be supposed to be arranged symmetrically around the metallic atom, so as to be situated at the corners of a regular octahedron (Fig. 4), the position of the chlorine atoms remaining undefined by Werner.

Other groups than NH_3 may be included in the first zone, in which case it is easy to see that isomerism becomes possible with compounds of the type

$$\left[Me \begin{matrix} A_4 \\ B_2 \end{matrix} \right] X_n$$

This hypothetical tetrahedral grouping permits the prediction of the possibility of two isomers, whose space formulae are not superposable: both such substances should therefore be optically active. By submitting to resolution certain compounds of the two types:

$$\left[\begin{matrix} A \\ B \end{matrix} Co\ en_2\right] \text{ and } \left[\begin{matrix} A_2\ Co\ en_2 \\ (Cr) \end{matrix}\right]$$

in which A or B represents Cl, Br, NH_3, NO_2, SCN or H_2O and en = ethylene diamine or two molecular radicles NH_3, Werner obtained isomers with a very appreciable rotation. In one isomer containing a single atom of cobalt, a specific rotation of 200° was obtained, whilst another with two cobalt atoms gave the very high value of 800°.

Some of these compounds maintain their optical activity unchanged in solution for several months, others exhibit a phenomenon akin to mutarotation. The substitution of certain components of the complex by different groups sometimes produces racemisation, whilst in others the activity is preserved. A few of these complexes give a very considerable rotary dispersion. The peculiar feature about the chromium compounds is that the value of the rotary power always lies about 150° below that of the corresponding cobalt compound, indicating that the metal must play the master rôle in the production of the activity. In his book, "New Ideas on Inorganic Chemistry" (translated by Hedley), Werner fully states the evidence in favour of his theory so far as it could be produced at the time when his book was published.

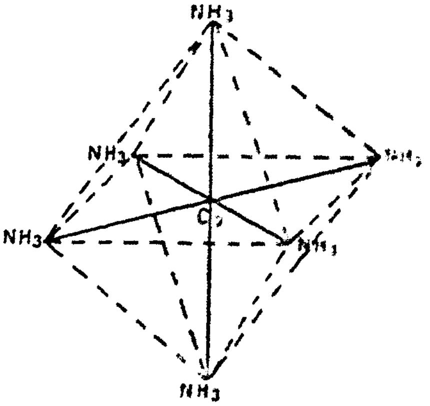


Fig. 4.

Werner[501] states that: "If, in accordance with (his) proposed structural formulæ, the elementary atoms forming the molecules have their valencies saturated, they must, nevertheless, have some unsaturated valencies, as only in this way is it possible to explain how the apparently saturated molecules can unite with each other to form molecular compounds. It was formerly the general belief, and even now this same view is largely held, that the structure of molecular compounds is unprovable as they consist of the combination of the molecules to form complexes quite apart from the relationship of the atoms concerned. Recent discoveries have, however, shown that this combination of molecule with molecule seldom, if ever, occurs, and that, even in molecular compounds, the combination is really between definite atoms. Hence, it is possible to devise structural formulæ for the so-called molecular compounds in the same manner as for the valency compounds."

The difference between the valency compounds and the molecular ones is due, according to Werner's co-ordination theory, to the valency compounds being derived from compounds in which the chief valencies are saturated, whilst the molecular compounds are formed by saturation of minor valencies. According to this theory the molecular compounds should be less stable than the valency compounds, yet this is by no means always the case : a very large number of the so-called molecular compounds being amongst the most stable substances known!

The representation of the constitution of the compounds under consideration by means of the H.P. theory overcomes the difficulty introduced by the use of major and minor valencies, as in Werner's theory, as the H.P. theory is one of valency compounds and not of molecular ones and is in full agreement with the high stability which has been observed.

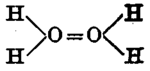
B. The H.P. Theory and the so-called "Water of Crystallisation"

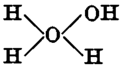
The frequent occurrence of 6 and 5 H_2O molecules in compounds containing "water of crystallisation" suggests that this water may be in the form of hexites or pentites and may thus form the foundation of a theory to explain the occurrence of water of crystallisation.

The view that the H_2O-molecules can form hexites and pentites requires a higher valency for oxygen than that usually ascribed to it. Various writers have shown that oxygen has, at times, a higher valency than 2, and the physical properties of water confirm this. Thomsen[502] has pointed out that the water molecules of salts often separate in pairs at the same temperature, from which he concluded that either the water molecules are arranged symmetrically about the molecule of the salt or the molecular weight of water is double that of steam. The latter view requires oxygen to have a valency greater than 2.

A number of other investigations imply that water is capable of becoming polymerised. Thus, Paternos' experiments[503] suggest that the molecular weight of water in acetic acid is 18 or 36, according to the solidifying temperature of the mixture. According to Eykmann[504], water in paratoluidine has one-half, but in phenol the full normal molecular pressure. Walker[505] has measured the heat of liquefaction of ice in ethereal solution and concludes that the molecular weight of water is 36. Ramsay and Aston[506] consider that water and some other substances containing hydroxyl, such as alcohol, acids, etc., are molecular aggregates when in a fluid condition.

[W. R. Bousfield and T. Martin Lowry[771] have advocated the view that liquid water is a ternary mixture of "ice molecules," "water molecules," and "steam molecules," these three varieties being perhaps identical with Sutherland's[772] "trihydrol." Armstrong[773] has added to this theory the conception of isomeric molecules, of equal size, but different structure. Moreover, Tamman[774] has prepared at least four polymeric forms of ice :

"dihydrone"  with

"hydronol" 

and so forth. Such extensions as these have been found to be necessary, in order to explain the experimental data that have been accumulated in recent years, and must now be regarded as essential parts of the theory of the constitution of water.

Even steam, so long considered as a uniform material that could be represented accurately by the much-beloved and greatly over-worked formula H_2O, has been shown by the careful measurements of Bose[775] to be a mixture of simple and polymerised molecules, e.g.

$$H_4O_2 \qquad 2\,H_2O$$

the proportion of the substance in the simpler form being reckoned at 91 per cent. in the neighbourhood of the boiling point.]

Kohlrausch and Heydweiller[507] and H. Ley[508] have found that the electrolytic dissociation of water is greatly increased on raising the temperature. The "acidity," which is very feeble at the ordinary temperature, increases to such an extent that at 100° C. it is almost equal in strength to that of phenol. This[509] is clearly shown in the following Table, in which *t* is the temperature, *d* the degree of dissociation and *K* the affinity coefficient :

t	*d*	*K*
0°	$0.35 \cdot 10^{-7}$	$0.12 \cdot 10^{-14}$
10°	$0.56 \cdot 10^{-7}$	$0.31 \cdot 10^{-14}$
18°	$0.80 \cdot 10^{-7}$	$0.64 \cdot 10^{-14}$
34°	$1.47 \cdot 10^{-7}$	$2.20 \cdot 10^{-14}$
50°	$2.48 \cdot 10^{-7}$	$6.20 \cdot 10^{-14}$

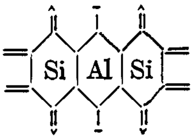
The strength (*K*) of the water increases considerably in the interval between 0° and 50°, and at 100° has a value at least a thousand times that at zero. This enormous increase in the strength at higher temperatures is explicable on the assumption that polymerisation occurs in the sense of the H.P. theory.

Assuming that oxygen has a higher valency than 2 and that water can form polymerisation products, the constitution of water-hexite and water-pentite may be represented graphically by :

$6\,H_2O \qquad 5\,H_2O$

which may be abbreviated to $\hat{H}$ or $\overline{H}$ or to ^ and –.

Such compounds may then be represented in more complex ones as follows :



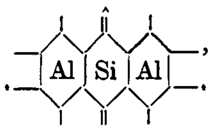
$$9\,H_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 4\,\hat{H} \cdot 2\,\overline{H}.$$

The bonds between the rings in this aluminosilicate are loosened by the manner in which the cyclic water (or water of crystallisation) is attached, and the position and mode of attachment of the water of crystallisation weakens or destroys the bonds between the base and the remainder of the molecule.

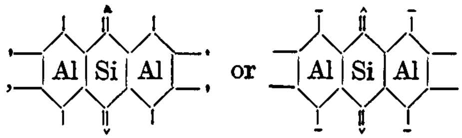
The Theory and the Facts

I. Hydro-aluminosilicates

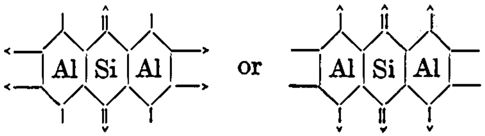
The structural formulæ shown below may be derived from the hydro-aluminosilicates given on page 105.



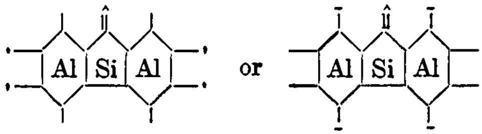
$H^{\circ}_{12}(\hat{Al} \cdot \hat{Si} \cdot \hat{Al}) \cdot 4\,\overline{H} \cdot \hat{H}$



$H^{\circ}_{12}\,(\hat{Al} \cdot \hat{Si} \cdot \hat{Al}) \cdot 4\,\overline{H} \cdot 2\,\hat{H}$



$H^{\circ}_{12}(\hat{Al} \cdot \hat{Si} \cdot \hat{Al}) \cdot 6\,\hat{H}$



$H^{\circ}_{10}(\hat{Al} \cdot \overline{Si} \cdot \hat{Al}) \cdot 4\,\overline{H} \cdot \hat{H}.$

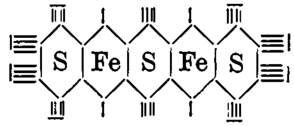
The position of the various water-rings implies (in agreement with theory) that these aluminosilicates are readily decomposed by acids.[510] A further study of these compounds must show that the easily separable water — the cyclic water — must be attached with varying degrees of strength.

II. Hydro-ferrosulphates

O. Kuntze[511] has studied the loss of water undergone by a mineral of the composition

$$6\,Fe_2O_3 \cdot 18\,SO_3 \cdot 62\,H_2O$$

at different temperatures. If the results obtained by him are calculated into formulæ, they agree surprisingly well with the structural formula :



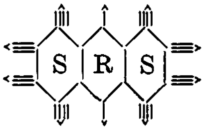
as may be seen from the following figures :

	Calcd.	Found	
40 H_2O	20.48%	21.04%	split off at 105° C.
8 H_2O	4.07%	4.05%	„ „ 110°
2 H_2O	1.03%	0.79%	„ „ 130°
8 H_2O	4.09%	4,06%	„ „ 140°
4 H_2O	2.05%	2.38%	„ „ red heat
6 Fe_2O_3	27.30%	26.86%	
18 SO_3	40.95%	39.01%	
		Al_2O_3 0.27%	
		Insoluble 1.79.	

This shows that the water pentites are split off at 105°, the weakly bound "water of constitution" of the SO_3 side-chains at 110°, the more strongly bound "water of constitution" of the middle SO_3-ring at 130°, the remainder of the "water of constitution" of the SO_3 side-chains at 140°, and the "water of constitution" of the iron-ring and the remainder of the water of the middle SO_3-ring at red heat.

III. The Water of Crystallisation in the Alums

In the light of the above theory of water of crystallisation, the alums possess the following structural formula :



$$3\,K_2O \cdot 12\,H_2O \cdot 3\,R_2O_3 \cdot 12\,SO_3 \cdot 10\,\hat{H}$$

From this structural formula it follows that :

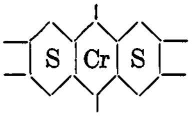
1. Five-sixths of the water (the hexite water) must be bound more loosely than the rest.

2. The bond between the rings on the one part, and between the rings and the base on the other, must increase with the amount of water split off.

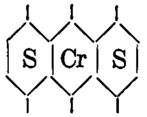
These consequences of the theory agree with the facts, as Van Cleef[512] has shown that the gradual and steady loss of water molecules which occurs in the alums when the heating is continued after five-sixths of the total water have been removed, is very noticeable. Recoura[513] and Whitney[514] have found that on heating chrome-alum

at 110° to constant weight, a new alum with new properties is obtained. This new compound is readily soluble in water, but, unlike the true alums, is not precipitated by barium chloride, i.e. the new compounds contain no SO_4-ions ; the bond between the SO_3 and Cr_2O_3 is strengthened by the loss of $\hat{H}$.

Water-free chrome alum may clearly occur in two isomeric forms as shown in the following structural formulæ :



A.
Ortho compound.



B.
Para compound.

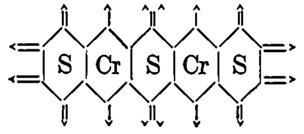
It is interesting to note that the free acids of this chrome alum have been prepared by both Recoura and Whitney.

A glance at the structural formulæ of the compounds *A* and *B* shows that these substances behave very differently in both chemical and physical properties. The basic or H-atoms in the ortho-compound are more easily separated than those in the para-compound. As a matter of fact, the ortho-compound (the green modification) has a measurable electrical conductivity, whilst the yellowish brown or para-compound shows no such conductivity.

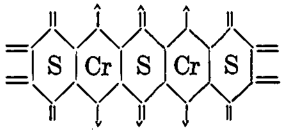
The lowering of the freezing point of the green acid (*A* compound) is 0.24°, that of the yellowish brown or *B* compound is 0.07°. According to Whitney the green modification can be converted into the yellowish brown one which, in aqueous solution, has the appearance of absinthe. It gelatinises after a few days.

IV. The Water of Crystallisation of Chromo-Sulphuric Acids

According to the new theory of water of crystallisation enunciated above, the two chromo-sulphuric acids studied by Recoura,* namely: $12\,H_2O \cdot 6\,Cr_2O_3 \cdot 18\,SO_3 \cdot 96\,H_2O$ (violet chromo-sulphuric acid) and $12\,H_2O \cdot 6\,Cr_2O_3 \cdot 18\,SO_3 \cdot 36\,H_2O$ (green chromo-sulphuric acid) must have the following structural formulæ :

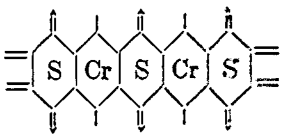


Violet Chromo-sulphuric acid.
A.



Green Chromo-sulphuric acid.
B.

* When chromic hydrate is dissolved in sulphuric acid the solution is at first green, but after a while changes to violet and deposits violet-blue, regular octohedra to which is ordinarily assigned the formula $Cr_2(SO_4)_3 15\,H_2O$, the proportion of water being somewhat uncertain. In the corresponding salts, the green variety gradually changes to violet at ordinary temperatures when in solution, but on boiling the violet changes rapidly into the green variety. It is generally stated that the green variety does not crystallise, and there is good reason to suppose that it is colloidal.—A. B. S.

or 

C.

A glance at the structural formulæ of the compounds *A*, *B* and *C* will show that the *A* compound must be less stable than *B* and *C* as it contains more water hexites. The Cr and S rings of the *B* and *C* compounds must be more strongly bound than those in compound *A*.

This consequence of the theory is confirmed by the discovery of Recoura, that the addition of barium chloride to the violet solution produces an immediate precipitate, whilst the green solution, when similarly treated, undergoes no apparent change.

The theory also explains the following behaviour of the green acid : In the air it appears to remain unchanged for several years, but its aqueous solution is very unstable and, on the addition of barium chloride, only a weak precipitate forms even after an hour. In time, a more labile bond is formed between the rings of the acid by the addition of water hexites.

If the nature of the separation of the water hexites in the *A* compound is compared with that of the ferrosulphuric acid, a definite analogy is observed. Here, also, the water hexites in the chrome and middle SO_3-rings are more firmly bound than the water hexites in the side SO_3-rings.

On heating to 90°, or more rapidly when boiled, the violet acid, or *A* compound, forms a green solution the composition of which, as Recoura's experiments have shown, has nothing in common with the solid green acid.

The fact that the colour of a compound can be changed by the addition of water to its molecule, closely agrees with the view that a change of colour may occur in a dilute aqueous solution on account of the combination of water hexites or pentites.

Recoura has studied the chemical reactions of the solution in a thermo-chemical manner. If increasing amounts of sodium are added to the green solution, the heat evolved on the addition of an amount of sodium equivalent to one-sixth of the sulphuric acid of the sulphate will be equal to the heat evolved when sodium combines with an acid, whereas all other proportions of sodium evolve much less heat.

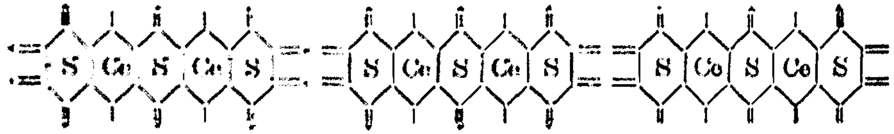
From this it follows that on boiling a compound of the type $\hat{S} \cdot \hat{Cr} \cdot \hat{S} \cdot \hat{Cr} \cdot \hat{S}$ it is converted into the penta-compound $\bar{S} \cdot \hat{Cr} \cdot S \cdot \hat{Cr} \cdot \bar{S}$ with resulting separation of three molecules of sulphuric acid. On treating the green sulphate $\bar{S} \cdot \hat{Cr} \cdot \bar{S} \cdot \hat{Cr} \cdot \bar{S}$ with $BaCl_2$ a very stable compound of the type $\hat{S} \cdot \hat{Cr} \cdot \hat{Cr} \cdot \hat{S}$ is formed, as already noticed in connection with other complexes, and according to Recoura only one-fifth of the penta-acid is precipitated.

If the mixture of green penta-acid is allowed to stand a long time, the penta- is converted into the violet hexa-acid. The penta-acid has not yet been prepared.

Whitney has tested Recoura's results by modern physio-chemical methods and has fully confirmed them.

Attention may also be directed, in this connection, to the hydrates of the cerium, praseodymium and neodymium sulphates studied by Rodig[515]. For instance, a concentrated solution of cerium sulphate at 25° forms the *duodecihydrate* $Ce_2(SO_4)_3\ 12\ H_2O$; between 30° and 40° C. the *octohydrate* $Ce_2(SO_4)_3\ 8\ H_2O$, and at temperatures above 74° the *pentahydrate* $Ce_2(SO_4)_3\ 5\ H_2O$.

The structural formulæ of these acids, according to the H.P. theory, are :



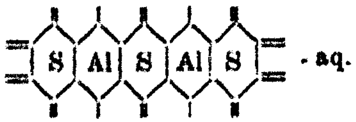
"Duodecihydrate." "Octohydrate." "Pentahydrate."

That the bond between the rings and the base is weakened by the addition of water radicles—hexite and pentite—is shown by the following facts :

1. According to an article in the "Papierzeitung"[516], two-thirds of the acid in a saturated solution of aluminosulphuric acid (366 g. aluminium sulphate per litre) may be neutralised with trinormal caustic soda solution, a permanent precipitate being formed. If the original solution is diluted ten times, only as much base is taken up as will correspond to one-third of the sulphuric acid.

From this it follows that in a concentrated solution all the H-atoms of the acid may be replaced by a base, but in a dilute solution only half of these atoms can be so replaced.

The structural formula of the aluminosulphuric acid under consideration is :



In a concentrated solution, 24 OH-groups are replaced by OR′, but only 12 hydroxyls are replaced in a dilute solution.

2. Gittelson[517] has found that by treating concentrated cerium solutions with concentrated phosphate solutions, salts are produced such as

$$3\ Na_2O \cdot 6\ Ce_2O_3 \cdot 6\ P_2O_5 \cdot 24\ H_2O,$$

but with dilute solutions of these substances free acids are produced.

C. The H.P. Theory and the Dissociation Theory of Arrhenius

It has been shown in the foregoing pages that the addition of cyclic water affects the bond of the rings and the ions. On the addition of water of crystallisation the bond between the rings is reduced and the ionisation increased. This fact is of great value in formulating a new theory of solutions. It leads to the "Dissociation Theory" of Arrhenius and gives it a new experimental basis.

According to Nernst[518], it is always questionable whether a molecule in solution adds water molecules or not, as the Raoult and van't Hoff methods give no definite results in this respect. Yet in view of the strong disdynamic action of water there can be no doubt that the dissociation of a solution of a salt on increasing dilution is accompanied by the addition of water.

Hence the fundamental law of van't Hoff in regard to solutions—viz. that in highly dilute solutions substances assume a condition similar to gases[519]—appears in a new light. Van't Hoff first suggested that the osmotic pressure of a solution (e.g. sugar in water) is as great as the pressure produced by an equal quantity of the dissolved substance if the latter were in the form of a gas occupying the same space as the solution. Yet no one had ever explained why dissolved substances should behave in this manner and no reason was known as to how the osmotic pressure was created. The authors' view (that an addition of water molecules to the molecules of the substance in solution occurs) indicates the existence of a definite attractive force between the molecules dissociated by the water and the water outside the semi-permeable membrane, and that that attractive force is the cause of the osmotic pressure.

Numerous other facts may be equally easily explained in the light of this new theory; amongst others are the formation of hydrates in solutions,[520] the presence of molecular aggregates in concentrated solutions and their destruction on dilution, e.g. the dissociation of the ether molecular aggregate $(CH_3 \cdot O \cdot CH_3)_n$, the aggregate $CH_3 \cdot CO \cdot NH_2$ in aqueous solution and several thermo-chemical phenomena.

The view that hydrates are formed in aqueous solutions is held by a number of authorities, some of whom have supported their opinion by experimental evidence, as: A. Werner[521], Abegg and Bodländer[522], Euler[523], Hantzsch[524], Lowry[525], Tournier d'Albe[526], Jones and his associates[527], V. Kohlschütter[528], Vaillant[529], R. J. Caldwell[530], H. E. Armstrong and J. A. Watson[531], E. H. Renni, A. J. Higgin and W. F. Cooke[532] and others.

A. Werner[533], as early as 1893, expressed his opinion that electrolytic dissociation is necessarily accompanied by the formation of a compound with the solvent used. "According to the results shown by our experiments," says Werner, "the existence of hydrates in aqueous solution is not merely an inference from the hydrate theory; these hydrates form an essential condition of electrolytic dissociation.

In an aqueous solution the ions are not metallic atoms, but metallic atoms combined with six water molecules, the whole forming definite radicles. This shows clearly why the electrical conductivity and the dissociation of a salt are so closely related to the solvent."

Abegg and Bodländer suggested that a hydration of the anions and cathions occurs. The degree of hydration of the alkali-ions increases in the following order: K, Na, Li, etc. Feebly dissociating solvents are those with feeble affinity for ions, and *vice versâ*.

Euler also adopted the idea of a hydration of ions taking place in aqueous solutions, and attributed to nickel, copper and cobalt ions the formulæ:

$$[Ni(H_2O)_4]^{++},\ [Cu(H_2O)_4]^{++} \text{ and } [Co(H_2O)_6]^{++}.$$

An acid in aqueous solution is, according to Hantzsch, a "hydronium-salt." The ions of hydrochloric acid in aqueous solution are, according to him:

$$HCl + H_2O = [H_2O,\ H]Cl = (H_3O)^+ + Cl^-.$$

This reaction is analogous to the formation of an ammonium salt from an acid and ammonia:

$$HCl + NH_3 = NH_3 \cdot HCl = (NH_4)^+ + Cl^-.$$

Lowry also regards the nature of electrolytic dissociation from the point of view of a hydration theory.

Tournier d'Albe touched upon the problem of hydrated ions in his work on the theory of electrons and expressed the opinion that each molecule draws molecules of the solvent to itself and becomes hydrated.

According to the most recent results published by Jones and his associates, the lowering of the freezing point of concentrated solutions shows, beyond a doubt, that hydrates exist in solution. Vaillant has definitely discovered the existence of hydrates in aqueous solution by means of spectrometric investigations.

R. J. Caldwell has shown that the speed of inversion of raw sugar by hydrochloric acid may be increased by the presence of various chlorides. To explain this phenomenon Caldwell supposes the salt to be hydrated in solution, a portion of the water thereby losing some of its solvent power, and thus effects a "concentrated" action on the sugar. To determine the "average hydration" of a given salt it is only necessary to ascertain experimentally how much water may be added to the salt solution in order to reduce the speed of reaction to its original amount.

H. E. Armstrong and J. A. Watson investigated the action of salts on the speed of hydrolysis of methyl acetate by nitric and hydrochloric acids. They found that in most cases the presence of a salt increased the speed and attributed this to the hydration of the salt.

E. H. Rennie, A. J. Higgin and F. W. Cooke examined the effect of various nitrates on the speed of solution of copper in nitric acid, and found that the presence of sodium nitrate, and particularly lithium

nitrate, caused a considerable increase in the rate of solution. Potassium nitrate was without effect and calcium nitrate and rubidium nitrate diminished the rate of solution. Beginning with the nitrate possessing the greatest accelerative power the salts may be arranged thus : Li, Na, K, Rb, Cs, which is the same order as Wymper found for their action on the speed of inversion of cane sugar, and these authors attributed it to the same cause, viz. the " concentrated action " which these salts possess on account of their hydration. The same authorities also conclude that the investigations mentioned form a further proof of the combination of the solvent with the dissolved substance.

The experimental investigations of a number of other authorities and the opinions expressed by them all point to the necessity of a complete agreement between any theory of " water of crystallisation " and any theory of " solution."

D. The H.P. Theory and the Constitution of Simple Acids

As the complex acids may be formed from simple ones, it must also be possible to form cyclic compounds including those in which an acid is not combined with other acids. A number of facts in support of this application of the new theory of the simple acids may be mentioned :

1. Tammann[534] prepared the following salts of a hexa-phosphoric acid :

$K_2Ag_4(PO_3)_6H_2O$,
$K_4Ag_2(PO_3)_6$,
$K_2Na_4(PO_3)_6$,
$K_4Na_2(PO_3)_6$,
$3\,[K_2Sr_2(PO_3)_6]\,4\,H_2O$,
$Li_2(NH_4)_4(PO_3)_6\;8\,H_2O$,
$Li_2H_4(PO_3)_6\;4\,H_2O$,
$Li_2Na_4(PO_3)_6\;6\,H_2O$.

And the following from a penta-phosphoric acid :

$(NH_4)K_4(PO_3)_5 \cdot 6\,H_2O$,
$(NH_4)Na_4(PO_3)_{56}$
$(NH_4)Li_4(PO_3)_5$,
$(NH_4)K_4(PO_3)_5$.

The following compounds, also prepared by Tammann, are also of interest, and are clearly related to a di-, penta-, hexa-phosphoric acid :

$Mg_6Na_4(PO_3)_{16}$,
$Ca_6Na_4(PO_3)_{16}$,
$Mn_6Na_4(PO_3)_{16}$.

From the theory of the constitution of complex acids formulated by the authors of the present volume, it follows that the hydroxyls of the hexa- or penta-radicles are partly acido- and partly baso-philic, i.e. the water they contain is not all bound to the radicles with the same

degree of force. This consequence of the theory also follows from the physio-chemical investigations of the above acids by Tammann.

In the compounds

$$(a) \quad K_2Na_4(PO_3)_6,$$

and

$$(b) \quad Na_2Na_4(PO_3)_6,$$

a positive current only removes one-third of the base.

By the prolonged action of $AgNO_3$ on $K_6(PO_3)_6$, Tammann was able to replace two-thirds of the base by Ag.

The behaviour of the compound $(NH_4)_5(PO_3)_5$ towards sodium and potassium shows that one-fifth of the base in it behaves differently from the remainder. The same is shown by the molecular conductivity of this ammonium salt and the conductivity of other salts obtained from it, such as :

$$(NH_4)(NH_4)_4(PO_3)_5,$$
$$(NH_4)Na_4(PO_3)_5,$$
$$(NH_4)Li_4(PO_3)_5.$$

If the absolute speeds of the ions are calculated by Kohlrausch's method (by the addition of the maximum values) the following maxima are obtained :

$(NH_4)(NH_4)_4(PO_3)_5$	$(NH_4)Na_4(PO_3)_5$	$(NH_4)Li_4(PO_3)_5$
$\lambda \infty = 300$	$\lambda \infty = 230$	$\lambda \infty = 210$

The maximum values actually found are for the ammonium salt 125, for the ammonium-sodium salt 96, and for the ammonium-lithium salt 90.

These figures can be most easily understood by assuming that one-fifth of the base passes away in the form of cathions whilst the remainder, with the acid, has the function of anions.

2. The hexitic structure of phosphoric acid in simple salts is shown in the following compounds, prepared by Glühmann[535] :

$$2\,BaO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 11\,H_2O,$$
$$2\,CaO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 6\,H_2O,$$
$$2\,CuO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 12\,H_2O,$$
$$2\,FeO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 12\,H_2O,$$
$$2\,MnO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 12\,H_2O,$$
$$2\,NiO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 24\,H_2O,$$
$$2\,CoO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 24\,H_2O,$$
$$2\,MgO \cdot 3\,Na_2O \cdot 3\,P_2O_5 \cdot 12\,H_2O.$$

In these compounds two-fifths of the OH-groups clearly behave in a manner different from the rest. Analogous compounds of niobic and tantalic acid with a small proportion of base have been obtained by Marignac[536] :

$$4\,H_2O \cdot 4\,K_2O \cdot 3\,Nb_2O_5 \cdot 12\,H_2O,$$
$$Na_2O \cdot 3\,K_2O \cdot 3\,Nb_2O_5 \cdot 9\,H_2O,$$
$$K_2O \cdot 3\,Nb_2O_5 \cdot 5\,H_2O,$$
$$4\,K_2O \cdot 3\,Ta_2O_5 \cdot 16\,H_2O,$$

$4\,Na_2O \cdot 3\,Ta_2O_5 \cdot 24\,H_2O$,
$4\,Ag_2O \cdot 3\,Ta_2O_5 \cdot 3\,H_2O$,
$4\,BaO \cdot 3\,Ta_2O_5 \cdot 6\,H_2O$,
$4\,MgO \cdot 3\,Ta_2O_5 \cdot 9\,H_2O$,
$4\,HgO \cdot 3\,Ta_2O_5 \cdot 5\,H_2O$.

3. The composition of the following compounds prepared by Hallopeau[537] shows the presence of hexites and pentites in some simple salts :

$5\,K_2O \cdot 5\,(NH_4)_2O \cdot 24\,WO_3 \cdot 22\,H_2O$,
$3\,(NH_4)_2O \cdot 3\,Na_2O \cdot 16\,WO_3 \cdot 22\,H_2O$,
$4\,(NH_4)_2O \cdot Na_2O \cdot 12\,WO_3 \cdot 14\,H_2O$,
$2\,Na_2O \cdot 3\,(NH_4)_2O \cdot 12\,WO_3 \cdot 15\,H_2O$,
$3\,(NH_4)_2O \cdot 3\,Na_2O \cdot 12\,WO_3 \cdot 22\,H_2O$,
$5\,K_2O \cdot 12\,WO_3 \cdot 11\,H_2O$,
$Na_2O \cdot 10\,WO_3 \cdot 21\,H_2O$, etc.

4. A number of oxygen-free salts have properties confirmatory of a hexitic or pentitic structure. Thus, the formulæ $CsCl_4I$, $RbCl_4I$, KCl_4I, $LiCl_4I$, etc., indicate the presence of pentite compounds. The formulæ KI_3, $CsBr_3$, $CsClBr_2$, $RbCl_2I$, etc., should probably be doubled and are then characteristic of hexites. Bredig[538] has discovered that in the compound KI_3 or, more correctly, K_2I_6 the group I_6 behaves like an independent ion, and is reminiscent of Tammann's investigations on the hexa- and penta-acids.

It is thus possible that free halogen acids, $H_2X_6(X{=}Cl, Br, I)$, may exist. The great solubility of chlorine in highly concentrated solutions of HCl led Berthelot[539] to the conclusion that, under such conditions, the compound HCl_3 or H_2Cl_6 is formed in a manner analogous to the production of K_2I_6 by the solution of iodine in potassium oxide. That a chemical compound is formed in this manner has been conclusively shown by the work of Le Blanc and Noyes.

E. The H.P. Theory and the Carbon Compounds

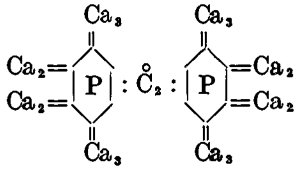
It may appear to be somewhat late to attempt to apply the H.P. theory to the carbon compounds in general, although the classical researches of Berzelius, Liebig, Kolbe and others[540] were made by men who sought for laws applicable to organic chemistry in those which applied to inorganic compounds. Nevertheless, a few facts may be pointed out which indicate that such an application of the H.P. theory is not without value.

Just as the aluminosilicates are converted into kaolin and may be produced from kaolin, so may the carbon compounds be converted into carbonic acid or may be formed from it. For instance, it is well known that plants take carbonic acid from the air and convert it into oxalic acid and the various kinds of sugar ; from these the animal fats and other complex organic compounds are formed. Oxalic acid is also a common product of the oxidation of both simple and complex

organic bodies. Thus, it is produced in varying amounts by suitably treating various carbo-hydrates, fatty acids, oils and glycerin : all the complex carbon compounds which can be oxidised by nitric acid.

Oxalic acid, like all inorganic acids, forms, according to Rosenheim[541], complex acids with other inorganic acids, hexites or pentites being produced under suitable conditions. A hexitic structure of oxalic acid is also found in a series of other compounds as in the cobalt oxalates mentioned on p. 256.

It is also important to note that carbonic acid can also form complexes with phosphoric acid, these complexes playing a large part in the formation of the bony framework of the animal organisms. According to Hoppe-Seyler (*vide* Scheff's "Handbuch d. Zahnheilk." 1909, 1, 362) the compound $10\,CaO \cdot CO_2 \cdot 3\,P_2O$ is contained in the dentine and enamel of natural teeth. To this basic carbo-phosphoric calcium salt the following structural formula may be assigned :



Thus, the chief constituent of dentine and of natural dental enamel has a chemical constitution similar to the β-complexes (p. 76), which are, as a rule, more stable than the α-complexes. This view of the structure of dentine and enamel makes it easier to understand the far higher resistance of the latter to acids than is possessed by calcium phosphate, and explains the strong combination of the carbonic acid and lime in the dentine. Without some such structural formula these properties are extremely puzzling.

When these facts, together with the figure 6 for the carbon atoms in the general formulæ for the sugars $n(C_6H_{12}O_6)—(n-1)H_2O$ and the genetic relationship between oxalic acid and the sugars are considered, the thought naturally arises that the transformation of oxalic acid into sugar by plants may possibly be due to both oxalic acid and the sugars possessing cyclic structures. In an analogous manner it is possible to explain the constitution of the sugar-like product obtained by Buttlerow[542] from formaldehyde and calcium hydroxide. This, according to Loew[543], is a single compound with the formula $C_6H_{12}O_6$; E. Fischer and F. Passmore[544] regard it as a mixture of various aldehydic or ketonic alcohols from which α-acrose may, in all cases, be separated. This α-acrose is, according to E. Fischer, closely related to the natural sugars.

A possible value of the H.P. theory may lie in its application to the formation of sugars from carbonic acid, as the assimilation of carbonic acid by plants is the chief reason for their existence as living organisms. The smallest observation which will assist in revealing the

secret methods by which plants effect this transformation is therefore of great importance.

Even if the existence of a large number of hexites and pentites in some carbon compounds may be considered doubtful, yet their presence in certain carbon compounds is highly probable. The latter, which are termed *aromatic* compounds, are well known to be different from those compounds which are in the form of open chains.

Kekulé[545] was the first to regard the aromatic compounds as derivatives of benzene. He conceived benzene as a closed ring of carbon atoms, the structural formula he suggested being the well-known hexagon which has been used so largely in the study of carbon compounds. This was the first hexite to appear in chemical literature.

Not only the constitution of the direct derivatives of benzene, but those of other substances more distantly related, such as napthaline, anthracene, phenanthrene, fluorescine and many other hydrocarbons, together with innumerable and important derivatives, have been studied with most useful results by means of Kekulé's theory and a greater knowledge of them has thereby been obtained.

The characteristics of the organic (carbon) pentites were first pointed out by V. Meyer[546] in his remarkable researches on thiophenes.

It is unnecessary to point out the great value of these beginnings of the H.P. theory in the development of organic chemistry and for industrial chemistry generally, for this is already well known. It is sufficient to state that Kekulé's benzene theory was the scientific foundation on which the methods of study and production of the most wonderful colours, valuable remedies, deadly poisons, pleasant scents, important anæsthetics, etc., have been based.

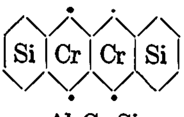
Hexite and Pentites devoid of oxygen

The H.P. theory indicates that carbon and silicon can form hexa- and penta-radicles which contain no oxygen. In this connection the researches of Manchot and Kieser[722] are of interest. These investigators have shown experimentally the existence of ring-compounds of silicon with chromium and aluminium, containing 6 Si-atoms. They consider that the behaviour of the compound Cr_2AlSi_3 towards HF and the consequent evolution of hydrogen shows that the molecular weight of this substance must be at least doubled and that the 6 Si-atoms of the compound $(Cr_2AlSi_3)_2$ are unquestionably united to each other. These investigators are thus the first to establish beyond all doubt the existence of hexa-silicon ring-compounds, and their work is an interesting confirmation of the H.P. theory.

It is also interesting to observe that in those chromo-hexites which are devoid of oxygen, one-third of the atoms behave differently from the others (pp. 269 and 292).

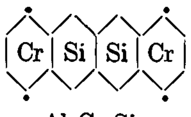
The structure of these oxygen-free compounds may be made clear by means of the following structural formula in which the Si-atoms are

directly united to other Si-atoms and chromium atoms with other chromium atoms, the Al-atoms being indicated by dots :



$Al_4Cr_8Si_{12}$

or



$Al_4Cr_8Si_{12}$

According to the H.P. theory, the molecular weight of this compound is at least twice as great as Manchot and Kieser concluded from their experiments.

When reviewing the German edition of the present work, Manchot[755] declared that the H.P. theory could not be extended beyond the chemistry of the silicates, but apparently did not have the above-mentioned experiments in his mind when he wrote : "That the complete neglect of this portion of the chemistry of silicon may lead to very erroneous conclusions in regard to the silicates, the reviewer[756] has shown on a previous occasion."

Manchot here refers to his criticism that Pukall's structural formula for kaolin, which has a double bond between the two silicon atoms (see page 111), is not in accordance with the behaviour of kaolin towards hydrofluoric acid : substances with united silicon atoms must evolve hydrogen when treated with HF, whereas kaolin does not.

It is very surprising that this critic instead of considering whether the H.P. theory of the constitution of aluminosilicates might not throw light on his own investigations, should accuse the authors of "a negligence which may lead to very erroneous conclusions." It appears that he has quite overlooked the support which his own investigations lend to the very theory which he condemns !

F. The H.P. Theory and the Constitution of the Atoms

The Archid Hypothesis.

In recent years an ever-increasing number of people have maintained that the atoms do not completely fill the space they occupy, but that they possess "parts." This view has long been held by those engaged in spectrolytic investigations, many of whom hold that the atoms slide over each other when emitting light ; some go so far as to say that some spectrum phenomena indicate a decomposition of the atoms. Some physicists even speak of the 'structure' of the atoms[547] and consider that it is by no means impossible to obtain further knowledge as to the internal structure of atoms, the special arrangement of their parts and the variations in the forces of these parts.

Those who are interested in the ionisation theory also speak of the "constituents" of the atoms, and, as the result of electrical investigations of gases, they consider that the negative electrons are really

constituents of what chemists have hitherto regarded as atoms and that these can be separated by electrical dissociation or ionisation with expenditure of different amounts of energy.

The hypothesis that the atoms contain "parts" has been particularly confirmed by the radio-activity of some elements discovered by H. Becquerel. According to Curie[548], Becquerel[549], Rutherford and Soddy[550], Re[551], Stark[552] and others, radio-activity is most satisfactorily explained by assuming atomic transmutations, i.e. the conversion of one atom into another or into several others.

The most recent investigations with regard to the chemical nature of the elementary atoms thus make the old hypothesis of the elements (which is the basis of alchemy) very probable. Moreover, it can scarcely be denied that Nature has produced her materials in accordance with unitary laws. It is, therefore, of interest to endeavour to discover the mysterious formation of the atoms from the elements.

A Hypothesis of the Constitution of the Atoms

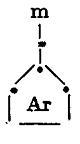
The smallest particles of an element may conveniently be termed *archids* (ἀρχή); the atoms may then be regarded as formed of archids in a manner analogous to that in which molecules are produced by the combination of a number of atoms. From five or six archid groups, *archid-pentites* and *archid-hexites* are produced respectively. Two or more archid-hexites or pentites may also combine directly or by the aid of other archids. In this manner α-, β- and γ- "archid-complexes" are formed in a manner similar to the atomic complexes.

The archidic radicles, like the atomic compounds, have archidic side-chains, and these limit the reactability of the archid compounds, viz. the atoms.

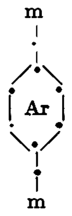
The combination of the archids occurs in accordance with archidic valencies, as in the formation of archid-hexite or -pentite, or of archidic radicles (hexite and pentite) and the addition and formation of archids as side-chains. These archidic valencies differ from the atomic valencies inasmuch as they cannot be determined by any existing methods. By the addition of long archid chains to the radicles or by the combination of archidic radicles with one another by means of archids with the simultaneous addition of long archidic chains, the archidic valencies are weakened and some must be set free, though these weak or free valencies cannot, at present, be definitely proved to exist.

The liberation of archidic valencies is usually accompanied by the evolution of electrical energy (radio-activity) and, after hundreds of years, results in a decomposition of the atoms or a transformation of them into one or more other atoms.

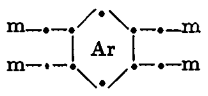
If the archids are represented by dots, the structure of the atoms may be represented, according to the new hypothesis, as follows:



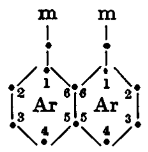
A.



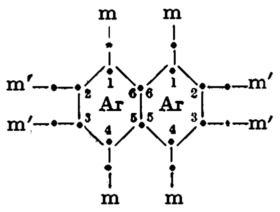
B.



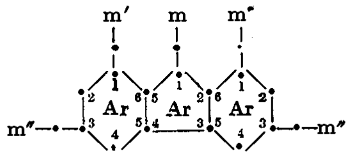
C.



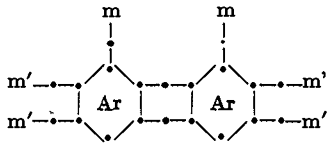
D.



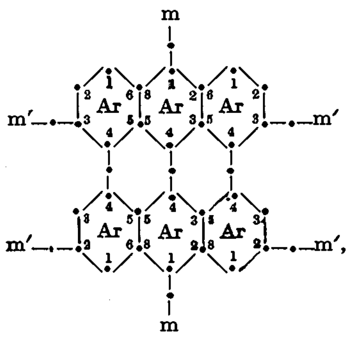
E.



F.



G.



etc. etc.

H.

The lines between the points indicate the archid valencies; the symbols m, m′ and m″ on the side-chains show the atomic valencies. Thus, the atom A is monovalent, B is divalent and E is octovalent.

The Consequences of the Archid Hypothesis and the Facts

(*a*) The Valencies of the Atoms.

According to the structural formulæ, the valencies of each of the atoms B, C and D must be of a similar kind, those of the atoms E, F, G and H, on the contrary, must be different. In atoms with side-chains

like E the valencies m must have a nature different from the valencies m′; in atoms with side-chains like F there must be three different kinds of valencies, viz. m, m′ and m″.

If, in atoms of the type F, the valency m is closed by treatment at a high temperature, m′ at a medium temperature, and m″ only at a lower temperature, these atoms would appear to have "variable" valencies and to be mono-, tri- or penta-valent. To the various positions of the side-chains in atoms of the F type may be due the possession of electro-positive properties by the valencies m and m′ and of electro-negative properties by the m″ valencies or *vice versâ*. Atoms with such side-chains can only unite with a definite number of electro-positive or electro-negative atoms or atomic groups.

From the structural formula F it may also be seen that, if the valencies m′, m, m′ and m″ are saturated and that one m″ side-chain is unsaturated, the atom will be capable of transformation into the tri- or penta-valent form, according to the power of the unsaturated valency.

If the valencies m′, m, m′ of the atom F are *strong* (i.e. if they are only affected by treatment at a high temperature) whilst the valencies m″, m″ are *weak* (i.e. only stable at low temperatures) the atom may be said to have three major valencies and two minor ones.

Atoms with side-chains such as H, in which part of the valency is only stable at low temperatures, may, in the light of this explanation, possess four minor valencies and two major ones.

The minor valencies cease to exist at other than low temperatures, in concentrated solutions and in substances in the solid state, so that they are usually overlooked. The authors have already (p. 228) stated that, according to Knoblauch and Nernst, spectrum analysis affords a very delicate means of ascertaining the constancy or otherwise of the constitution of a substance, as any change in the absorption spectrum of a dissolved substance indicates a change in the constitution of the latter.

Recently Hantzsch[553] has shown, as the result of a series of experimental investigations, that all changes in the spectrum effected by dilution are due to chemical causes and that each change in the spectrum indicates the progress of a chemical reaction. The delicacy of spectrum analysis is so great that the minor valencies will probably be discovered by its aid in many cases where they are, at present, unknown.

If, in atoms with four chief and two minor valencies (formula H), only two or three of the major valencies m′ are saturated, such atoms will have the power of saturating other m′ major valencies, whence atoms in which three major valencies are saturated must be more active in reaction than those in which only two major valencies are saturated. The former must be better able to pass into the tetravalent state than the latter, as the major valencies m′ are not symmetrically saturated.

These consequences of the archid hypothesis are in agreement with the known facts and experimental results.

In addition to atoms of constant valency, such as those of hydrogen, the alkali metals, alkaline earth metals, etc., there are atoms with variable valency such as those of N, As, Sb, P, Fe, Mn, etc.

For instance, in nitrogen atoms the side-chains are so arranged that the five resultant valencies are of unequal strength; three are stronger than the rest. The compound NH_4Cl, for example, is unstable at high temperatures and is decomposed in accordance with this difference of valency-strength into NH_3+HCl.

The reasons for the conclusions drawn from the structural formulæ just described are also confirmed by a study of nitrogen, as the atomic valencies of one and the same atom have different properties, some being electro-positive and others electro-negative. J. v. Braun[554] has pointed out this property of nitrogen and, according to him, a pentavalent nitrogen compound with several atoms or atomic groups is only formed when the five radicles necessary are not of one and the same chemical nature, but only when some possess electro-negative properties (like atoms and atomic groups which can act like anions of acid, as Cl′, Br′, I′ CN′, NO_2′) and others have electro-positive properties (as hydrogen, hydrocarbon residues and amido groups).

The correctness of this hypothesis is shown by the failure of all attempts to produce compounds in which the above condition is not satisfied, such as NCl_5, $N(C_2H_5)_5$. In this connection a recently discovered group of organic substances—the *porphyrexides*—is interesting. These are tetravalent derivatives of nitrogen in which the nitrogen shows a strong tendency to combine with hydrogen, and to pass into the trivalent state. This tendency must necessarily be due to a definite structure of the nitrogen atom.

Other atoms with variable valencies must also show an analogous behaviour. Recently, carbon has been placed among those atoms having a variable valency. The side-chains of some carbon atoms may be regarded as occupying positions represented by formulæ E (octovalent) and H (hexavalent) the carbon being then considered as possessing four major and two minor valencies.

If only two or three of the four side-chains are saturated, unsaturated compounds must be formed, as already explained, whence those with three saturated valencies must have a stronger tendency to be transformed into the tetravalent state than those with two valencies. Gomberg[555] has obtained compounds with trivalent carbon, and Nef[556] has prepared others with divalent carbon. In compounds in which only two valencies are in use, the carbon shows a much less tendency to pass into the trivalent state than in those in which three carbon valencies are saturated. Thus, whilst triphenylmethyl $C(C_6H_5)_3$, which was first prepared by Gomberg, can only be isolated with difficulty on account of its enormous power of reaction, compounds containing divalent carbon may readily be produced. These latter are powerful reagents, but are far less readily converted into compounds in which the carbon has four valencies.

The view that carbon may have more than four valencies does not agree with van't Hoff's hypothesis that the affinities of carbon act as though they were the lines connecting the centre of a regular tetrahedron with the four corners. According to this hypothesis, the carbon atom has a maximum of four valencies and no minor valencies. This is, however, in direct opposition to the proved existence of minor valencies apart from the four major valencies.

The physical isomeric properties of the "asymmetric" carbon atom (i.e. the one to which four different atoms or atomic groups are attached), such as optical isomerism, can be explained by means of the new theory (p. 312 *et sqq.*).

Schäfer's studies in connection with spectrum analysis[557] have provided new data respecting the minor valencies of carbon and some other atoms. Thus, striking colour-changes frequently indicate the presence of minor valencies, but they are best shown by certain organo-metallic compounds, particularly the complex salts investigated by Ley. The fact that many compounds of the heavy metals absorb normally whilst others vary greatly in this respect shows, according to Ley, that the metal in the latter case must possess minor valencies as well as the known major ones. The metal compounds of the amio acids and ketone acid-esters are interesting in this connection.

Schäfer thinks that a further proof of the existence of minor valencies is to be found in the pantochromism discovered by Hantzsch[558], i.e. the power of certain colourless salts or faintly tinted acids to combine with various colourless metals and form all kinds of colours.

Similarly, Schäfer considers that the presence of minor valencies is the cause of chromotropy, whereby many coloured compounds (chiefly yellow and red) may be produced from indifferent substances such as nitraniline, quinine and salts of polynitro-compounds.

The fact that water, alcohol, organic acids and other oxygen compounds have a greater molecular weight at lower temperatures than when in the gaseous state may also be best explained by the presence of minor valencies in the oxygen atoms.

A number of facts which seem to show that oxygen may have a higher valency than 2 have already been mentioned on page 259. Quite recently, observations have been made in connection with some organic compounds which appear to indicate the existence of higher valencies in oxygen. The most probable explanation is the presence of minor or weaker valencies of the oxygen. Amongst others who have written about the higher valency of oxygen—more particularly about its "tetravalency"—are Collie and Tickle[559], Baeyer and Villiger[560], Werner[561], Kehrmann[562], Gomberg[563], Walden[564], Walker[565], Sackur[566], and Cohen[567].

(*b*) Homologous Series of Atoms.

The monovalent pentites with the structural formula *A* (p. 275), the divalent archid-hexite radicle *B*, etc., can combine with *n* new

archid-hexites or pentites, or *m* archid-hexites and *m′* archid-pentites analogously to the atomic compounds, whereby a whole series of monovalent or divalent atoms are produced, as these new atoms only contain one or two side-chains. In this manner homologous series * may be formed which bear some resemblance to the homologous series in organic chemistry.

As there is a limit to the possible number of archid-hexites and -pentites, the weight of the atoms (atomic weight) of each homologous series must approach a definite limit.

Such homologous series of atoms are actually known, e.g. the halogen series, the alkali metals, the alkaline earth metals, etc. If these are arranged according to their atomic weights, the following series are obtained :

F = 18.90	Cl = 35.18	Br = 79.36	I = 125.90
Na = 22.88	K = 38.68	Rb = 84.80	Cs = 132.00
Mg = 24.18	Ca = 39.80	Sr = 86.94	Ba = 136.40

The differences between successive members of each series are :

16.28	44.18	46.54
15.80	46.12	47.20
15.62	47.14	49.46

The difference between consecutive atomic weights is constant, like that between members of other homologous series ; in this case it is either 16 or 16×3.

(*c*) The Causes of Radio-activity and the work of the Alchemists.

The radio-activity of some elements with high atomic weights, such as radium, uranium and thorium, is readily explicable in the light of the new hypotheses regarding the structure of the atoms. Assuming that these atoms have a structure analogous to that of the H-atoms, previously mentioned, i.e. that they are definitely γ-archid-complexes, their radio-activity may be readily explained as being due to their peculiar constitution. The property these atoms possess of radiating electrical energy is due to their structure.

From this it follows that only atoms with high atomic weights can be radio-active. This is actually the case.

The impossibility of increasing the radio-activity of the archid combination by existing methods of treatment indicates that enormous amounts of energy must be stored up in these compounds. Soddy[568] has published some interesting information on this point in a lecture

* When the members of a series of compounds are similar in constitution and chemical properties, but with the physical properties undergoing a gradual and regular variation as the molecular weight increases, the series is termed *homologous*, and the several members are said to be homologues of one another. There are many homologous series, especially among organic compounds.—A. B. S.

on "The Present State of Radio-Activity," in which the following words are particularly important:

"Radium evolves for every gram weight a hundred calories of heat per hour, and since in a year only one thousandth part changes, it follows that the total energy evolved in the complete disintegration of a gram of radium must be enormous. It is roughly about a million times that given out by a similar weight of coal burning. If the thirty milligrams of radium exhibited were all to disintegrate suddenly, the effect produced would equal the explosion of about a hundredweight of dynamite. Uranium in its complete disintegration produced radium, and hence the amount of energy evolved must be as much greater than in the case of radium as the whole is greater than the part. If we could artificially accelerate the rate at which radium or uranium disintegrates, we should on the one hand have achieved transmutation of a heavier element into lighter ones, and on the other hand have rendered available for use a new supply of energy a million times more powerful than any source at present known. The argument I have already stated shows that if we succeed in artificially transmuting uranium there is little doubt that the same means would be applicable to the other elements. Hence the supply of energy would be inexhaustible. But let us see what the old attempt of the alchemist involved. When he was concerned with building up a heavy element like gold from a lighter like silver, he was attempting a most profitless task. Frankly, even if it could be done, it would be impossible for it to *pay*. The energy absorbed would cost far more than the value of the gold produced. The energy of some hundreds of tons of coal would have to be put into an ounce of silver to turn it into gold. Energy possesses a market value no less than gold, as all who have to pay electricity bills realise. So we may dismiss this case. But where he was attempting to produce gold out of a *heavier* element like lead, the enterprise, if it had succeeded at all, would have been successful beyond the dreams of avarice. Not only would he have got the gold from lead, but also a store of energy would have been released in the change of far more intrinsic and commercial value than the gold. Not suspecting this, perhaps it was providential for him that he failed, or he might have realised the fate of the mythical chemist who discovered a new explosive the secret of which never transpired because the chemist and his laboratory disappeared simultaneously with the discovery. Actually, the alchemist in trying with his puny appliances to transmute lead into gold was attempting a task no less hopeless than that of a man attempting to destroy a battleship with a percussion cap. Even if sufficiently potent means are ever to hand to effect the transmutation of lead into gold, it is important to bear in mind that the gold would be a mere by-product, the energy rendered available would be the real gold-mine."

(*d*) Radio-activity as a Constitutional Property of the Atoms.

As radio-activity is due, according to the new hypothesis, to the structure of the atoms, it must also be quite independent of the chemical combination of the radio-active atoms with atoms of other kinds, as well as independent of the physical condition of the radio-active material, and must be impossible to prepare radio-active atoms artificially by either synthetical or analytical methods. The facts are fully in agreement with this consequence of the theory.

(*e*) The Transmutation of the Atoms.

From the authors' hypothesis it follows that it must be possible to convert one element A into another element B or to decompose one "element" into others.

This consequence of the theory has been proved by Sir William Ramsay's discovery that helium can be produced from radium and radium from uranium.

Section IV

The Extension of the H.P. Theory into a Stereo-chemical Theory, and the Combination of the latter with the Modern Theory of the Structure of Crystals

(*a*) Critical Examination of Existing Stereo-chemical Theories

NEITHER the H.P. theory in the form in which it is presented on pages 30–38 nor any existing theories dealing with structural chemistry can be regarded as satisfactory, as they do not take into account the fact that the atoms are divisible.*

The weakness of existing theories of structural chemistry has long been known and van't Hoff[569] was the first to suggest the importance of representing molecules by spatial diagrams.

Le Bel[570], quite independently, published a hypothesis concerning the spatial structure of atoms, but it received only scant attention at the time; those who took the most interest in it were the very men who endeavoured to disprove it experimentally.

J. Wislicenus[571] made both the above hypotheses the basis of a new series of experimental investigations.

This theory of spatial structure, which also deals with asymmetric

* Although the word "atom" really means "indivisible" its present use in chemistry may be conveniently retained, the word "archid" (p. 274) being used to indicate the smaller constituents.—A. B. S.

carbon atoms, has been supported by numerous and important results. It is also a noteworthy fact that all optically active organic substances, so far as their constitution is known, contain one or more asymmetric carbon atoms.

Similar speculations have proved very fruitful in the investigations on the sugars carried out by E. Fischer[572].

The work of Ad. Baeyer[573] on the isomerism of the hydrated phthallic acids also deserves special attention in this connection.

In addition to these theories various cases of isomerism of the nitrogen compounds have been examined in connection with their spatial relationships. The investigations of Werner and Hantzsch[574], Goldschmidt[575] and others are important in this respect.

E. v. Meyer[576] considers that the deductions from observations have been pushed as far as or even farther than is strictly legitimate. As he rightly remarks,[577] the greatest disadvantage of the existing stereo-chemical theories * is that they are only applicable to special cases and are not on a sufficiently broad basis. They form a convenient means of explaining a number of cases of isomerism, but cannot be applied to a general stereo-chemistry in the true sense of the words, to show the relationship between crystalline form and chemical composition, or to explain the various optical, thermal, electrical and other physical properties of crystals. These latter have been the subject of investigations by a number of mineralogists, including Schrauf[578], Fock[579], Becke[580] and others.

Schrauf considers that the atoms have definite axial positions in the molecules and that these form the basis of crystalline form. Schrauf's suggestions have not proved very fruitful and, according to Arzruni[581], who has criticised them, the principles and methods adopted by Schrauf are erroneous for this purpose.

Fock sought for a relationship between crystalline form and chemical composition in a combination of the results of modern stereo-chemistry and general crystallography. According to him, it is a positive fact that the affinities of the atoms do not merely have a definite value, but operate in a definite direction. "Crystallography teaches that the existence of a crystal is due to its general properties varying with the direction.

"The conception of direction is of different significance in the formation of crystals and in the chaining of the atoms, and leads to the thought that simple relationships may exist between the directions of the crystals."

P. Groth[582] states: "Crystals are usually characterised in their physical relationship by their being anisotropic, i.e. that none of their properties vary in intensity with the direction of the crystal in accordance with definite laws."

The simplest and most natural relationship which may be ascer-

* For further information on stereo-chemistry see No. 577 in *Appendix*.

tained from Fock's work is that the directions of the affinities in a "crystal molecule" reach the same symmetry as that of the crystal itself.

By "crystal molecule" Fock understands one of the molecules in the crystal, which produces an aggregate from the chemical molecules. The difference between a chemical molecule—which may be in the form of a gas or solution—and a crystal molecule—which is in a solid state—is shown, according to this writer, by the following facts:

1. Fluid or dissolved substances are chemically active; crystalline substances are never so.

2. Bases, acids and salts in a fluid state are electrolytes, but lose this property on crystallisation.

3. During crystallisation many substances take up "water of crystallisation."

4. Some crystals are optically active, but this property seldom remains when they are dissolved.

If the existence of large, independent atomic complexes in the crystalline state—crystal molecules—is assumed, the foregoing relationships are, according to Fock, capable of a simple explanation.

As Fock, in his stereo-chemical theory, knew of no plausible hypothesis by means of which the minimum molecular weight in the solid state could be explained, he could not bring his ideas—correct as they are—to a proper conclusion, and his stereo theory has therefore proved to be no more fruitful than that of Schrauf.

Whether a polymerisation of gas-molecules occurs when a gas passes into the fluid state, depends on the number of chemical molecules in a single crystal molecule. P. Groth[583] distinguishes between chemical and crystal molecules and, according to him, there is a number of facts which indicate that a crystal molecule is composed of a smaller or larger number of chemical molecules. Crystals thus correspond to the polymerised state as compared with the gaseous condition of single chemical molecules. Groth calls attention to Voigt's experiments on the elasticity of rock-salt, according to which the molecules of NaCl have a slightly different action in different directions—a behaviour which is incompatible with the view that the crystal molecule of rock-salt consists of one atom of chlorine and one atom of sodium.

Other writers, as S. Hunt, consider that calcite and quartz are aggregates consisting of 584 $CaCO_3$ and 948 SiO_2 respectively. A. E. Tutton considers that the molecular weight of the smallest crystals (crystal molecules) is either identical with that of the chemical molecule or that the crystal molecule does not consist of more than 1 to 5 chemical molecules. M. Bullouin concludes that crystal molecules may contain 4 to 5 chemical molecules. M. Herz[757] is of the opinion that the available experimental evidence is in favour of the existence of substances with the same molecular weights in the solid as in the gaseous state and of others which are polymerised.

Many attempts have been made to determine the molecular weights

of substances in the solid state by J. L. Vogt[758], Doelter and Vučnik[759]. All these endeavoured to determine the molecular weight of fused silicates by the aid of van't Hoff's formula :

$$t = \frac{m}{M} \cdot \frac{0.0198\, T^2}{q}$$

In this formula m represents the total number of grammes of silicate dissolved in 100 g. of the solvent, M the molecular weight of the silicate, T the absolute temperature, q the latent heat of fusion for 1 g. of the solvent and t the depression of the melting point. This method still leaves undetermined the question as to whether the crystal molecule has the same molecular weight as the substance in a fused or dissolved state.

Vogt sought to determine the molecular weights of diopsite, olivine and anorthite in this manner and concluded that they conformed to the following formulæ :

$CaO \cdot MgO \cdot 2\,SiO_2$ (Diopsite)
$2\,MgO \cdot SiO_2$ (Olivine)
$CaO \cdot Al_2O_3 \cdot 2\,SiO_2$ (Anorthite) ;

in other words, that there is no aggregation of molecules in these substances. These determinations of molecular weights have been determined in the same manner by Doelter and M. Vučnik[759], but these investigators reached entirely different conclusions and were of the opinion that the application of the van't Hoff formula to fused silicates is not free from objection, on account of the few determinations of q which have been made. The determinations of T are only reliable between 20° and 30°. It is not, therefore, surprising that Doelter and Vučnik found that the results obtained by this method disagreed with the formulæ in eight cases out of nine.

Doelter has not expressed any doubt as to the solid silicates being polymerised compounds, and he has, indeed, pointed out that if the van't Hoff formula is retained the results obtained from it agree much more closely with *multiple* than with single formulæ. According to Doelter, an extensive polymerisation occurs when aluminous silicates pass into the solid state, as is shown by the great heat of crystallisation.

Van't Hoff[761] has expressed the opinion that the solid state is not characterised by the formation of a complex molecular structure, but that in solid solutions the facts appear to show that the molecules are of the simplest possible constitution and not greater than twice the molecular weight ordinarily stated. This view is based on studies of isomorphous mix-crystals which it is assumed are in the state of solid solutions. *Positive* proof of the non-polymerisation of the molecules in solid solutions has not yet been published ; on the contrary, many facts are quite opposed to this view.

Becke[584] has criticised Fock's theory in a manner which demands

further investigation. According to him, in endeavouring to explain what relationship exists between crystalline form and chemical composition, special attention must be paid to symmetry as this is the most obvious factor common to both stereo-chemistry and crystallography. In Fock's theory this is not the case.

Becke's[585] attempt to explain stereo-chemically the cause of the hemihedrism * of calcspar and magnesite and of the tetrahedrism † of dolomite and ankerite is of special value. He started with the Bravais-Sohncke theory of crystalline structure, but instead of extensionless points he imagines symmetrical, corporeal molecules or molecular groups as forming a kind of lattice-work. Nevertheless, F. Becke has only been able to apply his partially developed ideas to a few cases, and as he has suggested no hypothesis to explain the minimum molecular weight in the solid state, his ideas do not admit of general application. According to L. Brauns[586], the method adopted by Becke in attempting to ascertain the relative position of the atoms in space may result in representing symmetry in the form of a stereochemical formula.

(*b*) The Modern Theory of Crystalline Structure and the Possibility of its Combination with Structural Chemical Theories

The work of Fock and Becke in connection with the formulation of a stereo-chemical theory would probably have been crowned with quite different results if the leading structural chemical theories were in as complete agreement with the available experimental material as is the case with the H.P. theory, or if the existing stereo-chemical theories had been placed on a broader basis. Hence it seemed worth while to endeavour to convert the H.P. theory into a general stereo-chemical theory and to combine it with the results of crystallography. This would appear to be the best method of solving the problem as to the relationship between crystalline form and chemical composition.

The fact that a series of physical properties of crystals shows a definite arrangement in the smallest particles, has stimulated a number of investigators such as Bravais[587], Frankenheim[588], and Sohncke[589] to attempt to find the laws connecting the theoretical spatial relations of observed crystalline forms to the corresponding symmetries.

If the limiting faces of crystals are conceived as lying in three axes which meet in a point but are not in a single plane, the crystalline forms of any substance may—as is well known—be expressed in terms of the lengths of these axes and of the angles between them. It is also supposed that the smallest particles of which crystals are composed lie along the same axes in accordance with definite laws, thus

* Hemihedrism is the formation of half the number of faces possessed by the complete forms of crystals of the same series.

† Tetrahedrism occurs when a crystal has only one quarter of the number of faces possessed by the primary form.

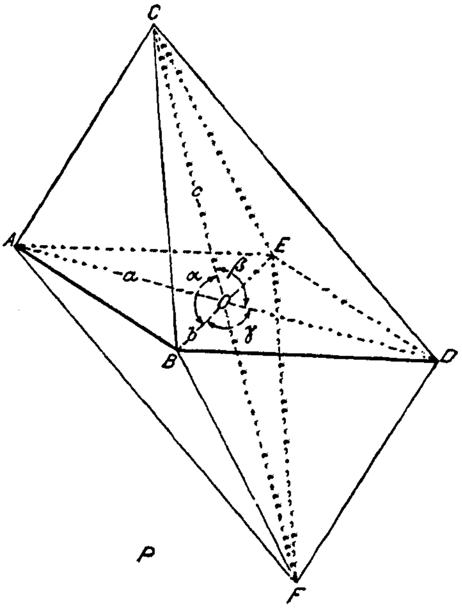
forming the various crystal forms. The generally accepted explanation of crystalline structure originated in this manner.

If this theory of crystalline structure is to be combined with a structural chemical theory, atoms or groups of atoms must, clearly, be conceived in place of the formless points. These points then become the centres of gravity of the various atoms or atomic groups. The place in which these "points" are found is their average plane of equilibrium, as the atoms and molecules are, as a result of their heat-content, in a state of constant, oscillatory motion.

None of the ordinary structural chemical theories can be combined in a simple manner with the general theory of crystalline structure. This combination is possible, however, as soon as the H.P. theory is extended into a stereo-chemical one.

(*c*) Stereo-hexites and Stereo-pentites, or a Stereo-chemical Theory

In a geometrical double pyramid of the form P:

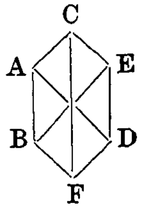


the two bases of the pyramids are identical.

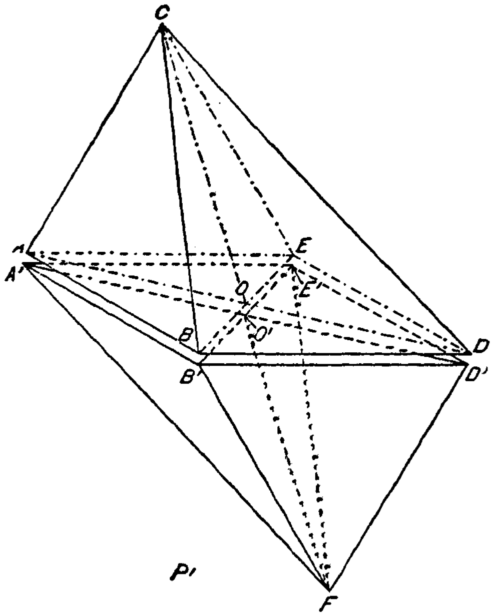
In this bi-pyramid P, CF is represented by *C*, AD by *A* and BE by *B*, the axes of which cut each other in *O*. The lines OA, OB and OC are represented by *a*, *b* and *c* and the angles COB, COD and BOD by *α*, *β* and *γ*. The axes CF, AD and BE are termed *chemical axes*, the ratio *a* : *b* : *c* is termed the "chemical parameter ratio" and the angles *α*, *β* and *γ* are termed the angles of the chemical axes.

In a given hexite, such as the compound 6 SiO_2, the atomic groups

SiO_2 may be arranged at each of the six corners of the double pyramid P. The valencies between the SiO_2 molecules are partly in the direction of the diagonals of the hexagon, i.e. in the direction of the chemical axes, and partly in the direction of the edges of the double pyramid. It is clear that in a hexagon only a portion of the possible valencies can be represented :



If the atomic groups of a pentite radicle 5 SiO_2 are supposed to be distributed in space, this must be doubled and a double pyramid P′

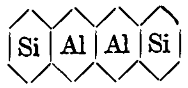


described in which the bases ABDE and A′B′D′E′ do not coincide, but are parallel to each other, though the distance between them is infinitely small. At the corners of this pyramid (P′), which possess a common chemical axis CF which cuts the other parallel chemical axes AD, BE and A′D′, B′E′ in the points O and O′, the atomic groups of two pentites are found.

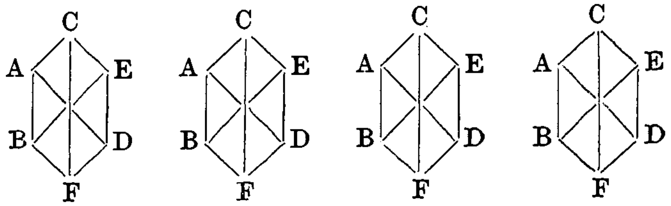
The straight lines OA, O′A′, and OB, O′B′ are each respectively

equal, and may be represented by a and b. The straight line OC is equal to O′F and may be represented by c. The pentites thus have a chemical parameter ratio $a : b : c$ and the angles of their chemical axes are analogous to those in the hexites α, β and γ.

A compound of the composition $6\,Al_2O_3 \cdot 12\,SiO_2$ may be represented diagrammatically by



or



i.e. the atomic groups in a molecule consisting of several hexites may be conceived as analogous to those of a hexite divided in space. The following facts should be observed :

1. All the atomic groups (Al_2O_3 and SiO_2) marked C and F in the compound in question are found on the axis CF, whereby each four Al_2O_3-groups, as shown by the structural formula, must lie near to each other, two pairs of SiO_2-groups, on the contrary, are further apart from each other.

2. All the atomic groups (Al_2O_3 and SiO_2) marked A and D are on the axis AD whereby the Al_2O_3- and SiO_2-groups are situated precisely the same as those on the axis CF.

3. The atomic groups marked B and E are distributed along the axis BE in an analogous manner as in 1 and 2.

4. Each six atomic groups—either SiO_2 or Al_2O_3—of the compound are bound by valency forces to their position in space, as is shown by the structural formula : special valency forces between the Ŝi- and the Âl-radicles are also in operation, as may be seen from the structural formula. With such an arrangement in space of the hexite units, it must clearly occur that the distances between the atoms of the two Al-hexites and of the two Si-hexites in the compound are unequal. Nevertheless, the difference in the distances between the atoms or atomic groups of the various Al- and Si-hexites is so extremely small that the different Al- and Si-hexites in the compound may be regarded as fully analogous.

5. A study of the aluminosilicates and allied chemical compounds shows that side-chains (basic, constitutional, water of crystallisation, etc.) may be attached in the direction of the axes CF, AD and BE.

6. If atoms or atomic groups occur at the point O (Fig. P), i.e.

in the point at which the three chemical axes cut each other, and are combined by valency forces with two, or n, hexites or pentites, the β- and γ-complexes are formed (pp. 76 and 241).

7. The chemical parameter ratio $a : b : c$ and the size of the angles α, β and γ form the chemical constants and depend upon the size of the valency forces between the atomic groups.

(*d*) The Hexite-Pentite Law

The valency forces between the hexite- and pentite-units and the radicles themselves (the hexites and pentites) of various substances are very variable; in many compounds they are so feeble that the existence of the hexite-pentite law has naturally been overlooked until the present.

It is highly probable that very many compounds (both simple and complex) of widely different elements, such as carbon, silicon, aluminium, iron, chromium, manganese, the halogens, nitrogen, oxygen, etc., exist in the form of hexites and pentites or in combinations of these—as has already been shown in the present work. This implies that this arrangement of the atoms is neither a mere coincidence nor a property of only a few substances, but of matter generally, and on this the hexite-pentite law is based and has proved to be of great value in stereo-chemistry.

The hexite and pentite form is not characteristic of only a few compounds (aluminosilicates, silico-molybdates, metal-ammonias, etc.) but of matter generally. Each chemical compound in the solid state is composed of hexites or pentites or combinations of them, the atoms or atomic groups being arranged in space in the manner indicated. In this manner major and minor valencies occur.

(*e*) The Combination of the Stereo-Hexite-Pentite Theory and the Modern Theory of the Structure of Crystals

The stereo-hexite-pentite theory mentioned above, and for the sake of brevity termed the "S.H.P. theory," may easily be combined with the theory of crystalline structure published by Bravais, Frankenheim and Sohncke, by substituting the units of hexites and pentites for the formless "points" in the latter theory.

Frankenheim[590], in his theory of the structure of crystals, has regarded these points as molecules from which the crystals form. Sohncke[591], in his theory of the atomic construction of matter, also used the word "point" as meaning "molecule." Sohncke sought to prove by *à priori* arguments that if the atomic construction of matter is the cause of the structure of crystals, only the present known systems of crystals can exist, no others being possible.

The hexite and pentite units are not equidistant from each other, as different affinities exist between them, especially if the substance under consideration is composed of units of different natures. The

distances between the various units, and particularly the differences in these distances, are so extremely small that they may be regarded as equidistant. If it is assumed that all the "molecular lines" AD, BE and CF, on which the hexite and pentite units are distributed, are in parallel groups (i.e. all the AD lines are parallel to all the AB lines and so on) and that the "molecular planes" ABDE and A′B′D′E′ are parallel to each other, the so-called "network" and "regular system of points," i.e. the theory of crystalline structure, follows.[592]

Limits of space prevent a more detailed description of the generally accepted theory of the structure of crystals; this can be obtained from the published literature on the subject. It may, however, be noted that this theory is generally accepted because it is in full agreement with numerous properties of crystals. Thus it was found, as a result of this theory,[593] that altogether 14 kinds of parallelopipedonal arrangements are geometrically possible and that only seven classes of crystals can exist which can be distinguished by their symmetry. This result is in agreement with experience. The seven different arrangements in space of the molecules show the same symmetrical ratios as the seven classes of crystals show in regard to cohesion.

It may be inferred *a priori* that, as this theory of crystalline structure does not postulate any bonds (affinity forces) between the units of the crystal, i.e. between the atoms or atomic groups, and pays no regard to the nature of these units, it cannot explain many of the constitutional properties of crystals. Thus, according to the "network theory" all crystals which crystallise regularly must be optically isotropic, yet such crystals are known which are optically diaxial, i.e. anisotropic. This theory also fails to explain other properties of crystals which are probably of a constitutional nature, such as the difference in behaviour of a crystal in two different positions such as is shown by its solution and change of temperature under the action of an electric current, and by the existence of two crystals built in opposite ways and polarising circularly in opposite directions. Sohncke endeavoured to explain this last property crystallographically by means of new hypotheses.

As previously explained, it is possible to combine the stereo-hexite-pentite theory with the modern theory of the structure of crystals. It is by no means improbable that the weaknesses in the modern theory of the structure of crystals may be overcome by its combination with the S.H.P. theory. To ascertain this it is now necessary to see how the facts agree with the S.H.P. theory.

(*f*) The Stereo-Hexite-Pentite Theory and the Facts

A. Di- and Poly-morphism and Hauy's Law

It follows from the theory that a given compound such as $CaCO_3$ may exist in either the hexite or pentite form if it is in the solid state. The minimum molecular weight of this substance when in the solid

state may therefore correspond to $(CaCO_3)_6$ or $(CaCO_3)_{10}$, or if both hexite and pentite radicles exist in the same molecule, other compounds, such as $(CaCO_3)_{16}$, $(CaCO_3)_{22}$, etc., are possible. The actual existence of simple acids and salts in the form of hexites and pentites has been shown in a number of cases in the chapter on "The H.P. Theory and the Constitution of Simple Acids" (p. 268). In the following formulæ, which may lead to a theoretical minimum of molecular weight, it will be found that simple salts may consist of hexites and pentites and their combinations :

In this connection the composition of the following borates[594] is interesting :

Boronatrocalcite	$Na_2O \cdot 2\,CaO \cdot 5\,B_2O_3 \cdot 12\,H_2O$
Ascharite	$6\,MgO \cdot 3\,B_2O_3 \cdot 2\,H_2O$
Pandermite	$2\,CaO \cdot 3\,B_2O_3 \cdot 3\,H_2O$
Colemanite	$2\,CaO \cdot 3\,B_2O_3 \cdot 5\,H_2O$
Franklandite	$Na_2O \cdot CaO \cdot 3\,B_2O_3 \cdot 7\,H_2O$
Hydroboracite	$Mgo \cdot CaO \cdot 3\,B_2O_3 \cdot 6\,H_2O$
Larderellite	$2\,(NH_4)_2O \cdot 8\,B_2O_3 \cdot 8\,H_2O$
Kaliborite	$K_2O \cdot 4\,MgO \cdot 11\,B_2O_3 \cdot 12\,H_2O$

The minimum molecular weight of some phosphates, arsenates and vanadates may be found from the composition of the minerals of the apatite group :[595]

Apatite	$9\,CaO \cdot 3\,P_2O_5 \cdot CaFl_2$ $9\,CaO \cdot 3\,P_2O_5 \cdot CaCl_2$ $9\,CaO \cdot 3\,P_2O_5 \cdot Ca(Cl, Fl)_2$
Pyromorphite	$9\,PbO \cdot 3\,P_2O_5 \cdot CaCl_2$
Polysphärite	$9\,R''O \cdot 3\,P_2O_5 \cdot CaCl_2$ (R''=Pb, Ca)
Mimetesite	$9\,PbO \cdot 3\,As_2O_5 \cdot PbCl_2$
Kampylite	$9\,PbO \cdot 3\,R^v_2O_5 \cdot PbCl_2$ (R^v=P, As)
Vanadinite	$9\,PbO \cdot 3\,V_2O_5 \cdot PbCl_2$
Endlichite	$9\,PbO \cdot 3\,R^v_2O_5 \cdot PbCl_2$ (R^v=As, Vd)

Hexites and pentites may also be formed from the molecules SiO_2, TiO_2, ZrO_2, Fe_2O_3, Al_2O_3 and from the atoms S, Se, P, C, etc. All these substances, when in the form of hexites or pentites, have, nevertheless, the empirical formulæ SiO_2, TiO_2, etc. Hence such hexites and pentites must be distinguished from each other by means of their crystalline form, hardness, specific gravity, behaviour towards reagents, etc. In a certain sense it may be stated that the substances $CaCO_3$, SiO_2, TiO_2, etc. are di- or poly-morphous ; in reality they form chemically different substances.

This consequence of the theory may be fully and completely proved by the facts. From the large amount of published information respecting polymorphous substances[596] the following may be quoted :

Calcium carbonate ("$CaCO_3$") : hexagonal-rhombohedric as calcite (calcspar),[597] rhombic as aragonite.[598]

Strontium carbonate ("$SrCO_3$") : dimorphous,[599]

Silica ("SiO_2") : hexagonal-trapezohedric-tetratohedric as quartz,

hexagonal as α-tridymite,[601] rhombic as β-tridymite. Von Lasaulx[602] and Schuster[603] have regarded β-tridymite as triclinic; Mallard[604], on the contrary, has shown that β-tridymite crystallises rhombically and Arzruni[605] and Groth[606] agree with him. Silica also crystallises regularly as α-cristobalite[607] and tetragonally as β-cristobalite.[608]

Titanic oxide (" TiO_2 "): tetragonal as rutile,[609] tetragonal as anastase,[610] rhombic as brookite[611] or arkansite and as edisonite.[612] Hautefeuille[613] has prepared anastase artificially at 860°, brookite between 860° and 1000° and rutile at a higher temperature.

Sulphur (" S "): rhombic,[614] α-monoclinic,[615] β-monoclinic,[616] γ-monoclinic (?),[617] hexagonal[618] and as " black sulphur."[619]

Ferric Sulphide (" FeS_2 "): regular pentagonal hemihedric as pyrite,[620] rhombic as marcasite.[621]

An interesting light is thrown by the S.H.P. theory on the cause of the dimorphism of the compounds with the empirical formula FeS_2. These sulphides may be compared with oxygen compounds from which the oxygen has been removed. For instance, the following compounds, with the ratio R : S = 1 : 2 are theoretically possible :

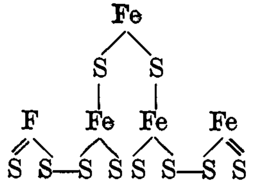
$$\begin{array}{ll} (a) & 1\tfrac{1}{2}\,R''O \cdot 3\,R_2'''O_3 \cdot 15\,SO_3 \\ (b) & 3\,R_2'''O_3 \cdot 12\,SO_3 \\ (c) & 3\,R''O \cdot 6\,SO_3 \end{array}$$

If the oxygen is struck out and Fe″ is substituted for R″ and Fe‴ for R‴, the following compounds will be produced :

$$\begin{array}{ll} (a) & 1\tfrac{1}{2}\,Fe'' \cdot 3\,Fe_2''' \cdot 15\,S = 7.5\,FeS_2 \\ (b) & 3\,Fe_2''' \cdot 12\,S = 6\,FeS_2 \\ (c) & 3\,Fe'' \cdot 6\,S = 3\,FeS_2 \end{array}$$

In other words, three different compounds with the empirical formula FeS_2 are possible. In the first, one-fifth of the iron must be present in the ferrous state, the remainder being ferric; in the second all the iron is in the ferric state, and in the third compound the whole of the iron is in the ferrous state.

According to Brown[622], only one-fifth of the iron in pyrite is in the ferrous state, whilst in marcasite it is all in this state, i.e. the structural formula *a* is that of pyrites, and *c* is that of marcasite. The *b* form of FeS_2 is not, at present, known. Brown assigns to pyrite the following improbable formula :



Other metals whose compounds occur in " ous " and " ic " states—such as cobalt, nickel, etc.—must form analogous compounds with the

general formula RS_2. In short, compounds with the general formula RS_2 must be di- or poly-morphous.

This treatment of the sulphides leads to new ideas as to their constitution, and it would be interesting, did space permit, to calculate the formulæ from the analyses of such compounds and to study their properties in the light of this theory.

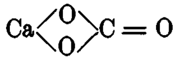
The simple elements Se, P, As, C, Sn, Zn, Fe, Ir, Pd, Ag, etc., occur in various forms, as do also the compounds: $(NH_4)_2SiFl_6$, K_2SnFl_6, ZnS, HgS, FeS_2, Ag_3SbS_3, Fe_2O_3, Sb_2O_3, As_2O_3, NH_4NO_3, KNO_3, $LiNO_3$, $Al_2O_3 \cdot SiO_2$, $Na_2O \cdot Al_2O_3 \cdot 3\,SiO_2$, $Na_2O \cdot Al_2O_3 \cdot 4\,SiO_2$, $K_2O \cdot Al_2O_3 \cdot 2\,SiO_2$, $CaO \cdot Al_2O_3 \cdot 2\,SiO_2$, etc.

According to the S.H.P. theory each chemical compound in the solid state must have its own definite $a : b : c$ ratio and its own α, β and γ angles; i.e. it must have its own crystalline form. According to this theory it is improbable that a single substance can change its crystalline form. This agrees in a remarkable way with the law stated by the well-known mineralogist Hauy[623] in 1801, to the effect that "one and the same substance, in a chemical sense, can occur in only one form."

Berthollet[624] opposed Hauy's view and suggested that the forms of crystals are accidental and are independent of their chemical composition. In support of this he referred to the two minerals aragonite and calcite, which have both the same chemical composition ($CaCO_3$), yet differ in crystalline form. Hauy next suggested that the difference in the crystalline form of these two minerals might be due to the presence of strontium in aragonite, though he failed to find strontium in some aragonites, and was eventually obliged to abandon this suggestion. In spite of opposition, Hauy refused to abandon his "law" and maintained that the calcspar-aragonite problem must be capable of some other explanation. Since 1821, however, Hauy's law has been neglected on account of the discovery, in that year, by Mitscherlich[625] of two forms of sodium phosphate $H_2NaPO_4 \cdot H_2O$.

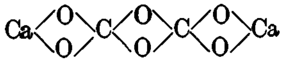
Mitscherlich[626] held that any substance—elementary or compound—can occur in two different crystalline forms. This view, which was based on the occurrence of two sodium phosphates with the formula $H_2NaPO_4 \cdot H_2O$ and of various elements in several forms, is clearly incorrect, as *de facto* these are chemically different compounds, all of which possess the same empirical formula.

It was only towards the close of the nineteenth century that a number of investigators concluded that Hauy's law is correct. Thus, Geuther[627] endeavoured to find the cause of the dimorphism of $CaCO_3$ in the existence of a "di-carbonic acid" $H_4C_2O_6$ and a "mono-carbonic acid" H_2CO_3; he assigned to calcite and aragonite the following structural formulæ:



Calcite.

and



Aragonite.

The credit for an explanation of di- or poly-morphism by means of an assumption which agrees with the S.H.P. theory is due to O. Lehmann[628]. This is based on numerous experiments. He concluded that the chemical molecules within the physical molecule are combined with each other—even though loosely; and that different modifications of a polymeric substance are really different substances.

As the result of his experiments, Lehmann was led to a "re-discovery" of Hauy's law which he stated in the following terms:

1. No substance has more than one crystalline form. If two substances have different crystalline forms they are different substances chemically, no matter whether they are atomic or molecular compounds.

2. No substance has more than one state of aggregation. The so-called "three states" of aggregation of some substances really represent three chemically different substances.

B. Isomorphism in the light of the S.H.P. Theory

Substances which are chemically related and those having an analogous constitution must clearly be related in their crystalline form. Such a connection between the crystalline form and chemical composition may be inferred from the S.H.P. theory, but its existence was discovered as early as 1819 by Mitscherlich[629]. Whilst examining phosphates and arsenates Mitscherlich observed that the salts of both phosphoric and arsenic acids frequently have the same form; he concluded that the chemical and crystalline forms are interdependent and proposed the term "isomorphism" for this phenomenon.

From the S.H.P. theory it also follows that isomorphous compounds have similar, but not absolutely identical chemical and geometrical constants ($a : b : c$ and α, β, γ). As the geometrical constants depend on the valency forces between the units and these vary with different units, the geometrical constants of analogously constituted substances which contain somewhat different constituents must clearly show certain differences. Hence, if the substances have not precisely the same composition they cannot be regarded as of identical crystalline form even though they are apparently quite isomorphous. Groth[630] has shown that, with more accurate instruments, the angles of crystals of isomorphous substances are found to be *very nearly*, but not absolutely, equal to each other.

The isomorphism discovered by Mitscherlich was found to occur in all mineral groups, and such minerals are therefore arranged into groups of crystallographically related substances. Amongst the most important of these are the widely distributed minerals of the felspar group, which have a remarkable resemblance to each other in their crystalline form and other physical characteristics. Schuster's[631]

investigations have shown that in a large number of felspars (plagioclases) the optical properties show these substances to be capable of arrangement in a definite series.

Under the name "tourmaline" are grouped a number of minerals which, with the instruments available, appear to agree completely in their crystalline form and are, therefore, regarded as isomorphous. Mica, clintonite, etc., form similar groups. Chemists and mineralogists have been very energetic in endeavouring to explain the isomorphism of such minerals in terms of chemical structure, but so far they have found no generally satisfactory solution to this problem. Thus, Rammelsberg[632], as early as 1850, pointed out a relationship between the monoclinic orthoclase and the triclinic minerals albite, oligoclase, labradorite and anorthite. According to him these minerals closely resemble each other in their geometrical form and do not differ from each other more than do other isomorphous substances. They also show a great similarity in their physical properties, but chemically they show such differences that "chemists consider that a separation is essential." On another occasion Rammelsberg[633] pointed out the similarity of the tourmalines crystallographically, though, according to him, they are quite unrelated chemically. In his opinion, the tourmalines consist of silicates of varying degrees of saturation which are combined in different ways and yet are isomorphous, i.e. they are of very similar form.

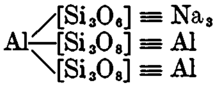
In order to explain the relationship between the crystalline form and the chemical composition of minerals of the felspar group, Tschermak assumed that the felspars were isomorphous mixtures of two silicates—albite and anorthite—to which he gave the following formula:

Albite ..... $NaAlSiSi_2O_8$
Anorthite ..... $CaAlAlSi_2O_8$

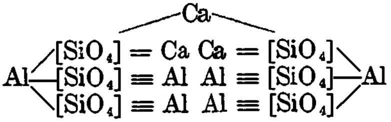
All triclinic felspars are, according to Tschermak, simply mixtures of albite and anorthite in all imaginable proportions, so that a continuous series is possible. Although this felspar theory has proved of great value for the systematic study of analyses of the felspars, it has been powerfully opposed from several sides. As a matter of fact, there is always some K, Mg, and ferrous and ferric iron in felspars which do not occur in the mixtures; i.e the felspars cannot contain these substances if they are simply mixtures of albite and anorthite. After prolonged discussion, extending over some years, Tschermak's theory is now accepted by most mineralogists, particularly since Schuster[634] has shown that the plagioclases may be made to form a series based on their optical properties and that for each composition of the limiting members there is a definite optical behaviour which is reminiscent of either albite or anorthite.[635]

As the miscibility of albite and anorthite—which are not analogous in their chemical composition—appears plausible from a chemical point of view, attempts have been made in other directions to find

structural formulæ for the mixed members of the felspars—albite and anorthite—so that they appear to have a chemical as well as a crystallographic relationship. For instance, Clarke[636] has suggested the following formulæ :

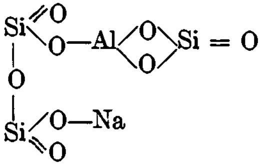


Albite.

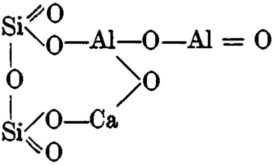


Anorthite.

Here he clearly assumes the possibility of an isomorphous replacement of the tetravalent groups (SiO_4) and (Si_3O_8). Groth[637], on the contrary, suggests the following formulæ for the same substances :

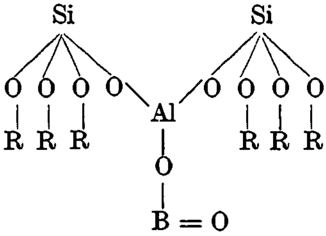


Albite.



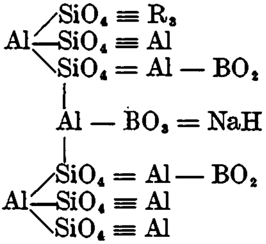
Anorthite.

Attempts have also been made to explain the relationship between the crystalline form and the chemical composition of the tourmalines on the assumption that hypothetical members of the series exist. Jannasch[638] has given the following simple formula for the "isomorphous mixture series" :

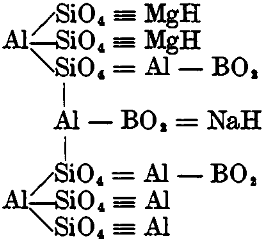


This does not agree with all the ratios of $SiO_2 : B_2O_3$ actually found in tourmalines. Clarke[639], on the contrary, assumes the following hypothetical members for the tourmaline series which are analogously constituted; these approach more closely to the actual facts :

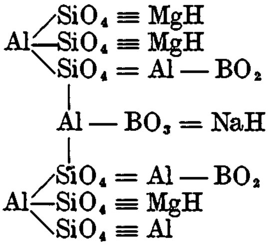
I.



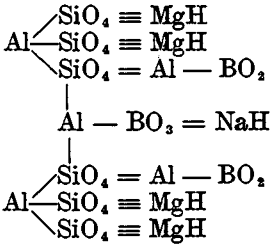
II.



III.

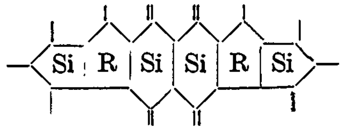


IV.

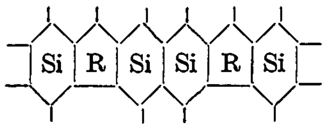


It is interesting to see what is the genetic relationship between all the members of the felspar groups, both crystallographically and physically, in the light of the S.H.P. theory. The calculation of the formulæ of a large number of analyses of the felspar group (see *Appendix*) shows that they may be regarded as salts of the following acids :

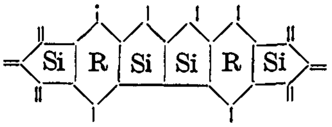
A.



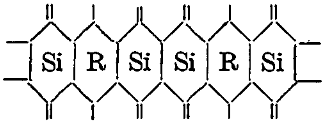
B.



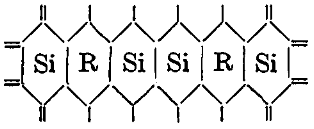
C.



D. (*a*)



D. (*b*)



i.e.

A. $8\,H_2O \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$
B. $7\,H_2O \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$
C. $9\,H_2O \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$
D. $12\,H_2O \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$

Two isomeric compounds D are shown ; isomers of the other hydrates are clearly possible.

As has already been shown, each of these types can produce a

whole series of hydrates. Strictly speaking, the formulated felspars of these different types are salts of various hydrates.

The hydrates here mentioned are, in a certain sense, the maximal hydrates of the felspars of these types, with a maximum proportion of "water of constitution" or of acid hydroxyls.

From this representation of the structure of the felspars the following inferences—which are in agreement with previous experiments—may be drawn :

1. There is a genetic relationship between the various members of the series, both physically and chemically, i.e. there is a similarity in their crystallographic, optical (see Schuster) and other physical properties.

2. The proportion of potassium, magnesium and iron (the last named in various states of oxidation) in some felspars is appreciable.

3. The maximum proportion of base + water of constitution in some felspars is explicable ; e.g. the presence in salt 50 of the A type of $6\,MO \cdot 2\,H_2O$; the presence of $7\,MO \cdot 5\,H_2O$ in No. 145 of type D and of $9\,MO \cdot 3\,H_2O$ in No. 146 of the same type (see *Appendix*).

4. These structural formulæ also provide an explanation how it is that if the content of base is divided as in formula *a* (C axis) a different system will be produced than would occur if the base were in the positions shown in *b* (i.e. nearer the A and B axes) ; i.e. the formation of monoclinic and triclinic felspars may be readily understood. The formula *b* is that relating to the triclinic felspars.

The general crystalline form of a large number of compounds, such as those of type *a*, is explicable by means of their common kernel or core.

Analogous relationships are also observable in the minerals of the tourmaline group (see *Appendix*).

It is interesting to note that Retgers[640] had previously suggested that the isomorphism of the members of various silicate groups may be completely explained by means of a large, common kernel or core. "If we regard them as containing such a molecular core, it is at once clear that the secondary atoms may be regarded as chemically analogous. No matter whether the molecules which adhere to the large core are small, like H_2O, CaO or NH_3, or whether they contain 6 or 7 molecules aq., the chief fact is that the common core reveals itself clearly in the crystalline form."

These opinions on the constitutions of the felspars, tourmalines, etc., were not without influence, for even simple compounds of which the analyses lead to simple formulæ have been regarded by many writers as though they were *mixtures*, i.e. as composed of substances mixed in capricious proportions and not combined in stoichiometrical quantities. Others have regarded substances as "isomorphous mixtures" even when they have shown them to be composed in definite stoichiometrical proportions. As an instance of this the "mix-crystals" of sulphurous salts investigated by Fock[641] may be

mentioned, particularly the ammonium salts $(NH_4)_2O \cdot S_2O_5 \cdot 1\frac{1}{2} H_2O$, and the salts with the general formula $R''O \cdot S_2O_5 \cdot \frac{1}{2} H_2O$ (where R''=Zn, Cd, Fe, Ni, Co and Mn) which Fock has examined crystallographically. In spite of the fact that these "mix-crystals" contain their various constituents in stoichiometrical proportions, Fock regarded them as "isomorphous mixtures."

The following salts were obtained by Fock :

I.	1.	$4 (NH_4)_2O \cdot ZnO \cdot 5 S_2O_5$
	2	$4 (NH_4)_2O \cdot FeO \cdot 5 S_2O_5$
	3.	$4 (NH_4)_2O \cdot NiO \cdot 5 S_2O_5$
	4	$4 (NH_4)_2O \cdot CoO \cdot 5 S_2O_5$
	5.	$4 (NH_4)_2O \cdot MnO \cdot 5 S_2O_5$
II.	6.	$3 (NH_4)_2O \cdot 2 CdO \cdot 5 S_2O_5$
III.	7.	$16 (NH_4)_2O \cdot 6 FeO \cdot 22 S_2O_5$
IV.	8.	$18 (NH_4)_2O \cdot 4 ZnO \cdot 22 S_2O_5$

On re-calculating Fock's figures the following Table is obtained :

Compound	$(NH_4)_2O$ per cent.	RO per cent.	$(NH_4)_2S_2O_5 \cdot 1\frac{1}{2} H_2O$ per cent.	$RS_2O_5 \cdot 1\frac{1}{2} H_2O$ per cent.	Total	Mol.-ratio
NH_4 · Zn-Salt						
(a) Tabular crystals	18.47	6.39	79.19	19.90	99.09	4 : 1
	18.64	6.44	79.93	20.07	100.00	
(b) Prismatic crystals	18.82	5.82	80.71	18.12	98.83	9 : 2
	19.02	5.92	81.57	18.43	100.00	
(NH_4) · Cd-Salt	14.34	16.40	61.50	38.36	99.86	3 : 2
	13.97	17.15	59.89	40.11	100.00	
NH_4 · Fe-Salt						
(a) Crystal from the solution	16.81	8.12	72.09	27.43	99.52	8 : 3
1 FeO : 1 $(NH_4)_2O$	17.11	7.88	73.36	26.64	100.00	
(b) Crystal from the solution	18.73	5.89	80.32	19.90	100.22	4 : 1
1 FeO : 4 $(NH_4)_2O$	18.77	5.77	80.51	19.49	100.00	
NH_4 · Ni-Salt	18.64	5.74	79.94	18.86	99.00	4 : 1
	18.73	5.97	80.34	19.66	100.00	
NH_4 · Co-Salt	18.69	5.73	80.15	18.86	99.01	4 : 1
	18.73	5.97	80.34	19.66	100.00	
NH_4 · Mn-Salt	18.41	5.63	78.95	19.23	98.18	4 : 1
	18.79	5.69	80.58	19.42	100.00	

The molecular ratios shown above differ slightly from Fock's ; he obtained a series corresponding chiefly to $4 (NH_4)_2O \cdot R''O \cdot 5 S_2O_5$.

According to him the geometrical ratios of these salts are :

Compound	a : b : c	β
NH_4 · Zn Salt	2.0597 : 1 : 1.2042	90° 52′
NH_4 · Cd Salt	2.1299 : 1 : 1.2263	90° 49′
NH_4 · Fe Salt	2.0564 : 1 : 1.1907	90° 51′
NH_4 · Ni Salt	2.0643 : 1 : 1.2077	90° 56′
NH_4 · Co Salt	2.0594 : 1 : 1.2045	90° 54′
NH_4 · Mn Salt	2.1289 : 1 : 1.2173	90° 19′

These figures do not indicate "isomorphous mixtures," but definite chemical compounds in which may clearly be seen the characteristic which is so often observed in pentites, viz. that one-fifth of the units behave differently from the remainder.

Rammelsberg[642] has also shown that the components of "isomorphous mixtures" have a relatively simple relationship to each other; from this he concluded that they must be regarded as molecular compounds with a simple and rational molecular ratio.

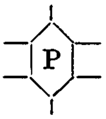
The influence of Tschermak's theory of the constitution of some felspars has been very great and some chemists and mineralogists have even used it to explain the crystallographic relationship between the members of a series of other complex silicates. In this way, the minerals of the scapolite group with its end-members consisting of mejonite $Ca_4Al_6Si_6O_{25}$ and marialite $Na_4Al_3Si_9O_{24}Cl$;[643] the amphibole group with actinolite $(Mg. Fe)_3CaSi_4O_{12}$ and syntagmatite $(R''_3R'''_2\text{-}Si_3O_{12})$[644] as end metals, the clintonite, mica, orthochlorite and other groups have been regarded as isomorphous or morphotropic[645] mixtures. No one appears to have been troubled by the thought that many of the so-called mix-crystals of this series are still unknown.

Rammelsberg[646] sharply protested against this generalisation of Tschermak's theory with which he did not agree, but he was unable to convince many people of the truth of his protest. It is clear that, if the Tschermak theory were correct, it would be of general application and would not apply to merely a single group of minerals,[647, 648] as is found to be the case. The great difficulty in the way of accepting the theory that these substances are isomorphous mixtures is to be found in some facts which this theory cannot explain and which are in direct contradiction to it. Thus, Retgers[649] endeavoured to produce mix-crystals from the salts KH_2PO_4 and $NH_4H_2PO_4$, and according to this theory he should have obtained an "unbroken series of mixtures." As a matter of fact, he was only able to obtain "mixtures" containing 100 to 80 per cent. of potassium salt to 0 to 20 per cent. of the ammonium salt, and 20 to 0 per cent. of the former to 80 to 100 per cent. of the latter. He could not obtain any intermediate compound containing 75 to 25 per cent. of the potassium salt and 25 to 75 per cent. of the ammonium salt. In endeavouring to prepare mix-crystals of $KClO_3$ and $TlClO_3$ the same investigator[650] again failed to obtain a continuous series. The crystals produced contained either 0 to 36·3 or 97·93 to 100 molecular per cents of the first salt. Between these limits of 36·3 and 97·93 there was a gap of nearly 62 molecular per cents. H. Schultze[651] in preparing mix-crystals of $PbMoO_4$ and $PbCrO_4$ has found that these only unite in certain definite proportions.

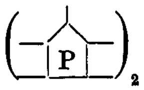
Negative results have also been obtained by several other investigators such as Wyrouboff[652] with $(NH_4)_2SO_4$ and $(NH_4)_2CrO_4$, Topsoë[653] with $BeSO_4 \cdot 4H_2O$ and $BeSeO_4 \cdot 4H_2O$. No explanation of these facts, which are in direct opposition to the theory of isomorphous mixed crystals, has yet been found. Yet these facts are not merely explicable by, but are direct consequences of the H.P. theory when the following are taken into consideration:

1. Tammann's chemical and physio-chemical investigations have

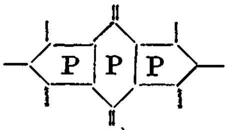
shown that, in accordance with the H.P. theory, the OH-groups in the hydrates



(a)
$3\,H_2O \cdot 3\,P_2O_5$



(b)
$5\,H_2O \cdot 5\,P_2O_5$



(c)
$5\,H_2O \cdot 8\,P_2O_5$

behave differently; in *a* $\frac{1}{3}$, in *b* $\frac{1}{5}$, and in *c* $\frac{2}{5}$ behave differently from the remainder (see pp. 268 and 269). For this reason Tammann was only able to obtain from the hydrate *a* the salts $Na_2O \cdot 2\,K_2O \cdot 3\,P_2O_5$ and $K_2O \cdot 2\,Na_2O \cdot 3\,P_2O_5$, and could not prepare $\frac{1}{2}\,Na_2O \cdot 2\frac{1}{2}\,K_2O \cdot 3\,P_2O_5$ and $\frac{1}{2}\,K_2O \cdot 2\frac{1}{2}\,Na_2O \cdot 3\,P_2O_5$ in this manner.

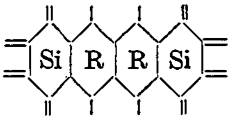
Further, in these alkali-salts of the hydrate *a*, only $\frac{1}{3}$ of the base conducts positive electricity and $K_4(PO_3)_6$ passes off as an anion.

In the compound $(NH_4)_2O \cdot 4\,(NH_4)_2O \cdot 5\,P_2O_5$, $\frac{1}{5}$ of the base behaves differently from the remainder (p. 269) both chemically and physio-chemically. Thus, only $\frac{4}{5}$ of the $(NH_4)_2O$ can be replaced by a base, the compounds $(NH_4)_2O \cdot 4\,R'_2O \cdot 5\,P_2O_5$ (R'=Na, Li) being formed; only $\frac{1}{5}$ of the base atoms conduct electricity. From the composition $3\,R''O \cdot 2\,Na_2O \cdot 8\,P_2O_5$ (R''=Mg, Ca, Mn) it may be seen that in the hydrate *c*, $\frac{2}{5}$ of the base behave differently from the rest.

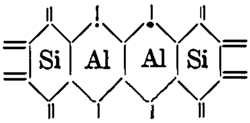
2. The minerals of the epidote group have the general formula:

$$2\,H_2O \cdot 8\,CaO \cdot 6\,R_2'''O_3 \cdot 12\,SiO_2 \qquad (R''' = Al,\ Fe),$$

and the structural formula:

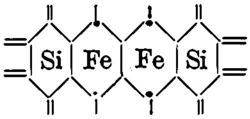


In the R-hexites, $\frac{1}{3}$ of the R-atoms must clearly behave differently from the others. As a matter of fact, the end-members of this mixed series (see *Appendix*) are:



$$2\,H_2O \cdot 8\,CaO \cdot 5\,Al_2O_3 \cdot Fe_2O_3 \cdot 12\,SiO_2$$

and



$$2\,H_2O \cdot 8\,CaO \cdot 4\,Fe_2O_3 \cdot 2\,Al_2O_3 \cdot 12\,SiO_2$$

Members with $5.5\,Al_2O_3 \cdot 0{\cdot}5\,Fe_2O_3$ or $5\,Fe_2O_3 \cdot Al_2O_3$ are unknown.

These facts lead to the conclusion that, in many cases, the production of a continuous series of mixtures without any gaps is chemically impossible. In this way the experimental results obtained by Retgers, Schultze, Wyrouboff, Topsoë and others may not only be explained, but can actually be predicted from the H.P. theory. For instance, Schultze's experiments on the production of mix-crystals from $PbMoO_4$ and $PbCrO_4$ lead to the result shown in the following Table:

Constituents	Mol. %	Mols.	Mol. %	Mols.	Mol. %	Mols.	Crystalline	Colour
$PbMoO_4$ and	74	12	66	4	58	3	tetragonal	red
$PbCrO_4$	26	4	34	2	42	2		
$PbMoO_4$ and	27	6	10	2	—	—	monoclinic	yellow
$PbCrO_4$	73	16	90	18	—	—		

Schultze thus obtained two series of salts which may be distinguished by their crystalline form and colour, viz :

I. 1. $16\,PbO \cdot 12\,MoO_3 \cdot 4\,CrO_3$
2. $6\,PbO \cdot 4\,MoO_3 \cdot 2\,CrO_3$
3. $5\,PbO \cdot 3\,MoO_3 \cdot 2\,CrO_3$
II. 4. $22\,PbO \cdot 6\,MoO_3 \cdot 16\,CrO_3$
5. $20\,PbO \cdot 2\,MoO_3 \cdot 18\,CrO_3$

The difference in the crystalline form and the colour of the crystals obtained from a mixture of $PbMoO_4$ and $PbCrO_4$ can be explained. These properties are closely related to the chemical constitution of these substances : the tetragonal form and red colour are characteristic of hexites and pentites in molybdenum compounds in which this metal is partly replaced by Cr, and the monoclinic form and yellow colour are natural to chromium hexites and pentites in which part of the metal has been replaced by Mo. There is also another good reason why Schultze could not obtain a continuous series of mixtures from lead molybdate and chromate, viz. in Mo- and Cr-hexites and pentites one portion of the atoms behaves differently from the others on substitution. This behaviour is clearly shown in the compounds obtained by Schultze.

The present fashion for considering that "isomorphous mixtures" are not chemical compounds is partly due to the influence of Berthollet[654], who, starting with the idea that chemical reactions depend on the masses present, reached the conclusion that in a compound consisting of two or more atoms the extent to which the reaction proceeds will depend on the number of atoms available, provided that no special conditions interfere with the mass-action.[655] From this conclusion, Berthollet argued that substances usually enter into combination in variable quantities according to the conditions under which the reaction occurs.

Proust opposed this view of Berthollet's and the difference between

them was eventually ended by the definite proof of the constancy of the combinations. It appeared, however, as if Nature had produced both "privileged" (combined in stoichiometrical proportions) and "unprivileged" compounds (isomorphous mixtures which are not combined in definite proportions and obey the mass-law of Berthollet). This is not the case; on the contrary, Nature has formed all definite compounds—including the so-called "mixtures"—according to one and the same law.

The following observations, made by John Hunter, with regard to the harmony and obedience to definite laws which are always found in Nature are well worth quoting here:

"How often we stumble against what we think are irregularities in Nature! How often we fancy that the chain is broken just because we cannot see each link in the chain and because the incompleteness of our knowledge prevents our seeing the symmetry of the whole! Whenever it is given to a man to see harmony where previously only discord was apparent, or to find a relationship where formerly it was only guessed at but could not be proved, then, in my opinion, is it the urgent duty of such an one to show the harmony he sees in natural phenomena. He should do this for many reasons, not the least important of which is that the discovery of such harmony gives us all courage to tread the path of Truth. The discovery of new harmony, however small, lifts for a moment the shadow which ordinarily overhangs the Truth and hides it from our gaze."

These golden words of so great a scientist often recur to the minds of the authors of the present volume, when they realise that, at last, it has been permitted to them to remove completely the artificial division set up by Proust, more than a century ago, when he divided matter into "combinations" and "dissolutions," the former including definite chemical "compounds" and the latter molecular "combinations" in which the proportions appeared to be so irregular as to be the sport of chance, i.e. substances which do not appear to obey the law of constant proportions.

Soon after Proust had set up this artificial division (i.e. his systematic classification of matter into compounds and "mixtures"), Berthollet opposed it and asked the following pertinent questions: "Wherein shall we seek the reason why the 'compounds' are formed by the uniting of their constituents in constant proportions, whilst in 'combinations' the ratios are variable and apparently due to chance? Is the force which effects the union of a metal with sulphur or oxygen different from that which forms more complex substances out of these simpler compounds?"

From the nature of these two questions it is clear that Berthollet was fully convinced of the essential unity of the natural law involved. There is an old philosophical dictum *natura non facit saltum*, quoted by Darwin in introducing his Theory of Descent, in respect of the Harmony which pervades the Cosmos, about which Newton wrote in so illumin-

ating a manner, and regarded by Berthollet, in his classical "Essai de statique chimie," as applying with equal truth to the world of atoms. This idea was so firmly fixed in the mind of Berthollet that he did not hesitate to oppose Proust's dualistic conception and to insist on the unity of the force of chemical attraction. At the same time, it is only fair to state that Proust himself recognised something of the truth in Berthollet's contention when he wrote: "I do not wish to press this matter unduly lest I lose my way in a place which is not too brightly illuminated by facts. The forces which produce both kinds of compounds may or may not be the same, but it is at least true that the results are so different that they must not be grouped indiscriminately, even though Nature itself has placed only an indefinite line between them."

Since it has been shown in innumerable cases that the law of constant proportions—which Proust applied to only a limited number of substances—is capable of indefinite extension since Dalton's discovery of the law of multiple proportions, the statement of Berthollet quoted above becomes increasingly important and efforts should be made with increasing earnestness to establish the general application of the Proust-Dalton law. Even if this cannot yet be accomplished because of the many substances, such as glass, colloids, etc., which are regarded as solid solutions, it does not prove exceptions to natural laws, for no such exceptions can exist; it is merely the incompleteness of chemical theory which prevents the natural laws involved from being properly understood or defined so far as these apparent exceptions are concerned.

It is certainly surprising that none of the critics have pointed out this advantage of the H.P. theory, and it is even more remarkable that Allen and Shepherd should consider it a drawback of the theory. Thus, they state in their review of the German edition of this work:[737] "An important fact in this connection has been . . . completely overlooked. We are now in possession of many facts which show that it is never wise to assume that silicates are chemical compounds. For instance, to take a well-known example, the felspars are solid solutions and any theory of structure to be complete must show the permanency which is characteristic of the properties of true compounds as distinct from the maxima and minima of mere groupings." These critics further state that: "The authors never distinguish, and this is most important, between purely chemical changes and changes of an entirely physical nature."

The reply to these statements is that there is no need specially to distinguish between chemical compounds and the so-called isomorphous mixtures or solid solutions, as the distinction is perfectly clear! It would also have been much better if the critics had quoted at least a few of the "many facts which show that it is never wise to assume that silicates are chemical compounds," so that the precise value of this statement of theirs might be ascertained. As only the felspars are mentioned, any criticism must, for the moment, be restricted to these.

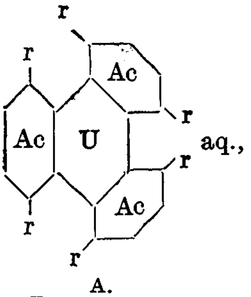
Now, on studying the structural formulæ of the felspars (p. 297) carefully, it is easy to see that almost without exception they are referable to one type. These formulæ also show how various substances in other groups of siliceous compounds can be formed from the felspars or *vice versâ* ; they indicate the physical relationship of all these compounds with reference to crystalline form, optical properties, specific gravity, etc. On the other hand, the assumption that felspars are "solid solutions" explains none of these things. How can Allen and Shepherd explain in the light of their theory of solid solution the properties of felspars which are described in paragraphs numbered 2, 3 and 4 on page 298 ? For what reasons should the felspars be treated in a different manner from other silicates and not regarded as definite chemical compounds ? Is the force which, in the case of certain silicates, forms definite chemical compounds, different from that which forms the so-called "solid solutions" from simple silicates ?

Many fights between chemical dualism and monism have occurred in the past and the victory has always been completely in favour of monism. Sooner or later, the dualistic conception of the constitution of compounds, which was published by Proust more than a century since, will go the way of all other dualistic theories.

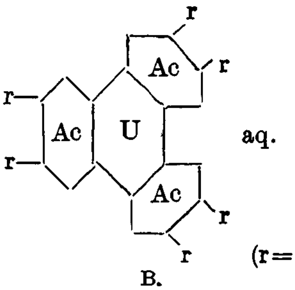
C. The Dependence of the Geometrical Constants on the Side-chains

It has been repeatedly shown in previous pages (*cf.* p. 216) that the addition of bases, "water of constitution" or "water of crystallisation," in the form of side-chains to hexites or pentites weakens the bond between the units forming the hexites or pentites, whilst their removal or splitting off strengthens the bonds. In other words, by adding bases in the form of side-chains, part of the valencies in the ring or core is destroyed. According to the S.H.P. theory, this must influence the geometrical constants $a : b : c$ and α, β and γ. Crystallographic experiments, previously made, are in agreement with this consequence of the theory.

The influence of the "water of crystallisation" on the crystalline form of a compound has long been recognised ; thus, the metallic sulphates with 5 H_2O are known to differ in form from those with 7 H_2O. In this connection a series of uranium-acetates prepared by Rammelsberg[656] are interesting. These have the general formula :



or



A. B. (r=½ RO)

$3\,RO \cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot aq.$ $3\,RO \cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot aq.$
R = Mg, Zn, Ni, Co, Cd, Ca, Sr, $(NH_4)_2$, K_2, Ag_2.

Of the possible compounds of this series, Rammelsberg prepared the following :

					$a : b : c$
I.	3 MgO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	12 $\hat{H}$	rhombic	0.7468 : 1 : 0.5082
	3 MnO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	12 $\hat{H}$	,,	0.7536 : 1 : 0.4957
II.	3 MgO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	7 $\hat{H}$	,,	0.8946 : 1 : 0.9924
	3 ZnO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	7 $\hat{H}$	,,	0.8749 : 1 : 0.9493
	3 NiO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	7 $\hat{H}$	,,	0.8670 : 1 : 0.9500
	3 CoO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	7 $\hat{H}$	,,	0.8756 : 1 : 0.9484
III.	3 MnO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	6 $\hat{H}$	,,	0.6330 : 1 : 0.3942
	3 CdO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	6 $\hat{H}$	,,	0.6289 : 1 : 0.3904
IV.	3 CaO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	6 $\hat{H}$	,,	0.9798 : 1 : 0.3865
	3 SrO	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O \cdot$	6 $\hat{H}$	,,	1 : 0.3887
V.	3 $(NH_4)_2O$	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O$		,,	1 : 0.4708
	3 K_2O	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O$		,,	1 : 1.2830
	3 Ag_2O	$\cdot 6\,UO_3 \cdot 9\,(CH_3CO)_2O$		,,	1 : 1:5385

The results of crystallographic investigations of these urano-acetates are in remarkable agreement with the S.H.P. theory.

The theoretical possibility of two series (A and B) of these urano-acetates is confirmed by the existence of two series of compounds (III and IV) with 6 $\hat{H}$ and with a different $a : b : c$ ratio.

If the series I and II are compared it will be seen that on the loss of 5 $\hat{H}$ the c-axis is largely increased, being, in fact, almost doubled.

A specially interesting example of the change in the geometrical constants effected by adding or subtracting side-chains is found in the *humite* series studied by Penfield and Howe, to which attention has been drawn by P. Groth[657], who assigns to them the following structural formulæ :

Prolektite	$[SiO_4]\,Mg\,[Mg(F.\,OH)]_2$
Chondrodite	$[SiO_4]_2Mg_3[Mg(F.\,OH)]_2$
Humite	$[SiO_4]_3Mg_5[Mg(F.\,OH)]_2$
Clinohumite	$[SiO_4]_4Mg_7[Mg(F.\,OH)]_2$

From the composition of these minerals it follows that each member of the series differs from the previous one by SiO_4Mg_2. The addition of this group always effects a definite change in the c-axis whilst the parameter $a : b$ remains practically unchanged.

The geometrical constants of these compounds are :

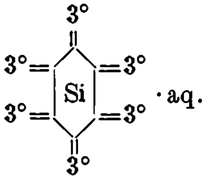
Prolektite	Monocl. prism.	1.0803 : 1 : 3 × 0.6287	90° 0′
Chondrodite	,, ,,	1.0863 : 1 : 5 × 0.6289	90° 0′
Humite	Rhomb. bipyr.	1.0802 : 1 : 7 × 0:6291	
Clinohumite	Monocl. prism.	1.0803 : 1 : 9 × 0.6288	90° 0′

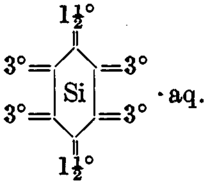
There is here a surprising regularity which may be expressed in the form of a "law": the *c*-axes of these minerals are in the ratio of 3 : 5 : 7 : 9.

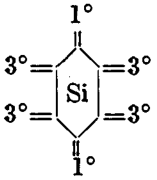
According to the S.H.P. theory, and assuming the fluorine to be replaceable by OH, the formulæ of these compounds are:

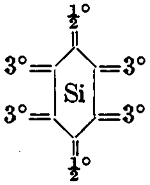
Prolektite	$18\,MgO \cdot 6\,SiO_2 \cdot 6\,H_2O$
Chondrodite	$15\,MgO \cdot 6\,SiO_2 \cdot 3\,H_2O$
Humite	$14\,MgO \cdot 6\,SiO_2 \cdot 2\,H_2O$
Clinohumite	$13\,MgO \cdot 6\,SiO_2 \cdot 1\frac{1}{2}\,H_2O$ (approx.)

The structural formulæ of these compounds will then be:


Prolektite.


Chondrodite.


Humite.


Clinohumite.

In the compounds of the above series, the addition to or separation of MgO only occurs in the direction of the *c*-axis. It is, therefore, clear why only the *c*-axis undergoes a regular change, the ratio *a* : *b* remaining practically constant.

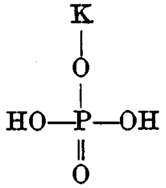
Of special interest are the *topical parameters* suggested by W. Muthmann[763] and F. Becke[764] for comparing the chemical and crystallographic properties of substances. These topical parameters are a combination of the crystallographic parameter with the molecular volume; they are derived from the spatial relations of the substances concerned and show the relative distances of the molecules from each other.

W. Muthmann has determined the topical axial ratios of the following salts, to which he assigns the formulæ:

KH_2PO_4
$(NH_4)H_2PO_4$
KH_2AsO_4
$NH_4H_2AsO_4$

and considers that the OK- or ONH_4-groups, the residual O atom and the OH-groups are attached to the P atoms symmetrically in the chief plane of symmetry.

J. H. van't Hoff[765] endeavoured to explain the data obtained by W. Muthmann by means of the following structural formula:

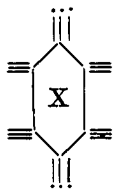


in which the vertical line represents the main axis *c*. The substitution of NH_4 for K increases the length of this axis, whilst the substitution of As for P effects changes in the dimension in every direction. This formula of van't Hoff's does not permit the data obtained by Muthmann to be predicted, nor does it show any relationship between analogous phenomena.

In accordance with the H.P. theory, Muthmann's formulæ should be multiplied by 6, so as to give:

A. $(KH_2PO_4)_6 = 3\,K_2O \cdot 6\,H_2O \cdot 3\,P_2O_5$
B. $(NH_4H_2PO_4)_6 = 3\,(MH_4)_2O \cdot 6\,H_2O \cdot 3\,P_2O_5$
C. $(KH_2AsO_4)_6 = 3\,K_2O \cdot 6\,H_2O \cdot 3\,As_2O_5$
D. $(NH_4H_2AsO_4)_6 = 3\,(NH_4)_2O \cdot 6\,H_2O \cdot 3\,As_2O_5$

In each case the formula represents the minimum molecular weights. The structural formulæ of the salts should be as follows: *R* representing K or NH_4, the bonds with dots indicate OK-groups and the bonds without dots the OH-groups.



$3\,R_2O \cdot 6\,H_2O \cdot 3\,X_2O_5$

This structural formula permits the following predictions to be made: 1. The space between the molecules must increase or diminish in the same or almost the same proportion in all directions within the crystal, if *P* as a whole is replaced in the ring by *As* or, conversely, *As* by *P*, as the bond between the vertical and the horizontal axes is influenced in the same manner. 2. The space between the molecules can only change in the direction of a single axis, viz. the vertical or main axis, if, in a phospho- or arseno-salt, potassium is replaced by ammonium or *vice versâ*, as these atoms are attached in the direction of the vertical axis.

It is remarkable how fully the investigations of Muthmann confirm the consequences of the S.H.P. theory.

According to Muthmann the space between the molecules is increased in all directions in the crystal in almost exact proportion, if the phosphorus in the phospho-salts mentioned above is replaced by arsenic. The increase is practically the same with ammonium and potassium, but if the potassium atom in potassium phosphate or arsenate is replaced by an ammonium atom, the centres of gravity of the units composing the crystal become more widely separated solely in the direction of the main axis.

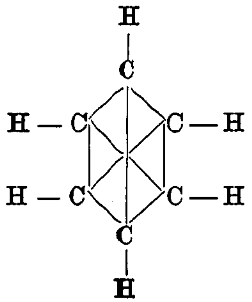
The Structural Formula of Benzene according to the S.H.P. Theory

From a study of the crystalline form of the benzene derivatives, P. Groth[659] has discovered "laws" which are reminiscent of the humite, phosphate and arsenate series previously described. The crystallographic investigation of a series of benzene derivatives has shown that there are certain atoms and atomic groups which replace hydrogen in benzene and its derivatives whilst only slightly altering the crystalline form, so that the form of the new substance may be compared with the original one. The change is of such a nature that, e.g. in rhombic substances, the ratio of two parameters ($a:b$) remains almost constant (with the small difference which all isomorphous bodies show, as is the case with the humite series), whilst only the third axis—the c-axis—undergoes a notable change in value. The atomic groups OH and NO_2 act in this manner. It is probable that the substitution of a hydrogen atom by these groups in benzene and its derivatives occurs in the direction of the c-axis. An energetic reaction accompanies the substitution of a hydrogen atom in benzene and its derivatives by Cl, Br and CH_3 which systematically changes the crystalline system into a less regular one. This may be due to substitution in the direction of the a- or b-axis and not in that of the c-axis.

A large number of other examples might be given to show that the addition of side-chains to (or their separation from) the molecule results in a change in the geometrical constants of crystalline substances.

In connection with the foregoing arguments a few words respecting the structure of benzene according to the S.H.P. theory are of interest.

The structural formula of benzene * deduced from the S.H.P. theory resembles the "diagonal formula" of Claus[660], viz.:



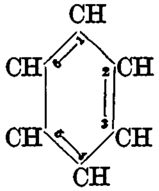
but one fact deserves prominence: according to the S.H.P. theory the six hydrogen atoms in benzene do not all behave alike, ⅓ of them (on the c-axis) acting differently from the rest (on the a- and b-axes). This consequence of the S.H.P. theory agrees with Groth's discovery

* The reader who wishes to refresh his memory will find an excellent statement of the ordinary theories of the constitution of benzene in "Organic Chemistry," by W. H. Perkin and E. Stanley Kipping, and in most text-books on organic chemistry.—A. B. S.

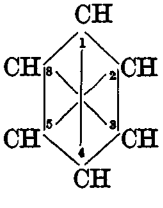
that if the hydrogen atoms on the *c*-axis are substituted only these are changed, whereas substitution of the hydrogen atoms in the *a*- and *b*-axes is accompanied by a notable change in the system of crystallisation. If, on the contrary, all the hydrogen atoms in benzene are assumed to be alike, Groth's discovery becomes inexplicable.

There is a more direct proof that one-third of the hydrogen or carbon in benzene behaves differently from the rest in chemical reactions, viz. the results of the investigations of Stohmann[661] and his associates on the heat of combustion of the aromatic compounds and their hydration products. These showed that the heat-values change continually in the decomposition of di-hydro compounds, whilst the increase in energy on the entrance of the first two hydrogen atoms in the benzene ring is notably greater ; i.e. one-third of the carbons in benzene behave differently from the rest.

That Kekulé's formula for benzene needs modification is also clear from the following: Ladenburg[662] was the first to point out that Kekulé's formula



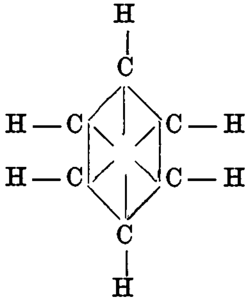
implies the existence of at least four bi-substitution products.[663] Of these, three are the derivatives at the points (1, 2), (1, 3) and (1, 4), including the assumed symmetry of the positions (1, 3) and (1, 5). There is also at least one series of derivatives in the position (1, 6), as this position is notably different from the position (1, 2) on account of the double bond between the carbon atoms in the position (1, 6). Claus[664] therefore suggested the following formula for benzene :



He argued from this that there are two kinds of valencies in benzene, viz. (a) those in compounds produced from the periphery of the hexagon, and (b) those formed from the diagonals of the hexagon. From this structural formula—which resembles that suggested for benzene by the S.H.P. theory—the existence of only three di-substitution products of benzene is explained, and this number is that actually found by experiment.

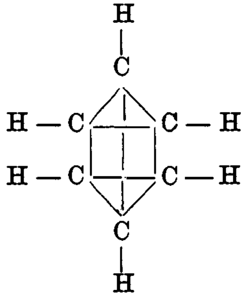
Another formula which represents the structural formula of benzene

in a manner very similar to the S.H.P. theory is the *centric formula* devised by Armstrong[665] and v. Baeyer[666] :



which is really a modification of Claus' formula. Von Baeyer has also proposed a centric formula with spatial representation.

Ladenburg's *prism formula*



was one of the first stereo-chemical formulæ for benzene. Other stereochemical formulæ have been devised by R. Meyer[668], Thomsen[669], Sachse[670], Schmidt[671], Vaubel[672], Hermann[673], Diamant[674], etc.

It has frequently been pointed out in the foregoing pages that the bond between the units of hexite and pentite radicles is weakened by the addition of side-chains (see p. 216, etc.). From this it follows that benzene and its derivatives must be more stable than hydrobenzene and the hydro-derivatives of benzene. This consequence of the theory is confirmed by the facts. The hydro-derivatives of benzene have been shown by the investigations of v. Baeyer to differ considerably from those which are not hydrated. For instance, di- and tetrahydro-derivatives were shown to have a marked olefine character. Thus, phthalic acid is completely resistant to potassium permanganate solution, but the di-hydrophthalic acids are oxidised by it. The benzene nucleus is not sensitive to hydrobromic acid and oxidising agents, but this resistance does not exist in the hydro-benzenes.

The stability of benzene—which has been proved experimentally—is in direct contradiction to Kekulé's formula.[675]

That a close relationship exists between compounds of the aliphatic

and aromatic series (*cf.* p. 270), as may be inferred from the S.H.P. theory, has been proved by the work of Schiff[676], Lossen and Zander[677], Horstmann[678] and Brühl[679]. From this it must be seen that the formation of hydro-derivatives of olefinic and aromatic compounds is analogous.

D. The Optical Properties of Crystals and the S.H.P. Theory

The physical properties of crystals are well known[680] to bear a very close relationship to their morphological characters. Light, heat and electricity operate in complete agreement in crystals, and the crystal systems arrange themselves in the same manner. This may be used as an argument in favour of grouping according to the optical, thermic, magnetic and other properties of crystals. Hence, if the optical properties of a crystal are known, it may be stated that each geometrical plane of symmetry of a crystal is also a physical one and that two crystallographic equivalent directions have also a physical relationship.*

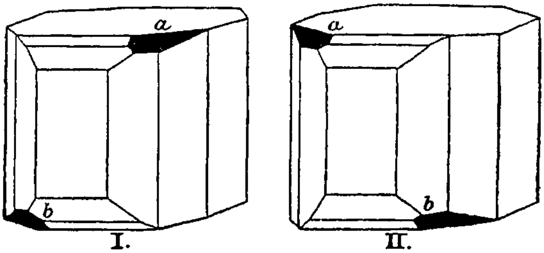
There are, however, exceptions to this rule: some crystals, for instance, are regular and their physical properties indicate no isotropic construction. In this connection the optical characters of crystals are frequently curious. An interesting example of this is found in the alum crystals: as substances which crystallise regularly they should be optically isotropic, but Brewster[681] showed in 1816 that the alums have a double refraction. Biot[682], who has still further studied these characteristics of the alums, confirms this view. The double refraction of the alums has also been studied by Reusch[683], E. Mallard[684], F. Klocke[685], Brauns[686] and other observers. Several explanations have been offered to account for their abnormal behaviour. The ordinary theory of crystalline structure neither affords an explanation nor does it give anything whereon one may be founded. Mallard[687] endeavoured to explain the anomaly crystallographically by assuming a special structure of the alum crystals, and regarded them as consisting of several individuals of lower symmetry than that of the whole crystal. Although several mineralogists have expressed their sympathy with this view, others, such as F. Klocke[688], disagree with it. Klocke considered that the optical anomalies of the alums are due to a "state of tension," but he regards the question as still open.

No less interesting is the cause of the rotation of the plane of polarised light shown by some crystals; there is ample reason for referring this to the chemical constitution of the crystals. This hypo-

* Von Federow has recently prepared a Table, comprising no less than 10,000 substances, the crystals of which have been adequately measured by skilled crystallographers. By means of this Table, von Federow declares it is possible to identify any substance included in it when the crystals have been properly measured. The Table is not available for general use, but in the hands of Prof. Federow it has proved very successful. A brief account of Federow's theory is given in Tutton's "Crystallography and Practical Crystal Measurement" (Macmillan).—A. B. S.

thesis is confirmed by the enantiomorphism of the circular polarising substances.

[Enantiomorphous crystals are those which have the same relation to each other as an object has to its mirror-image, as will be seen by holding the sketch of crystal I before a mirror, when the darkened faces, *a*, *b*, will appear as in the sketch in crystal II viewed directly, and *vice versâ*.]



I. II.

Enantiomorphous Crystals.

As early as 1848, Pasteur[689], in studying optically active tartaric acid and the optically inactive racemic acid, discovered this relationship between crystalline form and optical activity. Groth also regards optical activity as entirely due to the structure of the smallest particles of circular polarising crystals. He considers that if this optical property is characteristic of the crystal molecule itself, the solution must be saturated in order to produce optical rotation; as, unless the particles in solution have a complexity comparable to that of the crystalline molecules, no separation of the substance in a crystalline state can possibly occur. With many substances, however, this is not the case ; for instance, solutions of sodium chlorate show no optical rotation, but only those crystals whose forms are such that they are mirror-images of each other.

An apparently complete proof of this view is found in the interesting observation of Reusch[690] on the production of circular polarisation in mica plates. According to Reusch, if a large number (12–36) of uniform thin plates of bi-axial mica are laid one above another so that the plane of the (vertical) optical axis of each plate is turned to the right through an angle of 120° with respect to the plate below it, this combination of plates turns the plane of polarisation of a vertical beam of light to the right, the combination behaving, in a polarisation apparatus, in a manner similar to a plate of dextro-rotatory quartz cut vertically to the axis. If the mica plates are turned through an angle of 120° in the opposite direction, the combination is laevo-rotatory.

Pasteur's discovery respecting the crystalline forms of optically active tartaric acid and the inactive racemic acid, the fact that some substances only show circular polarisation effects when in the solid state, and the property of the mica sheets discovered by Reusch, all show that there is undoubtedly a relationship existing between optical activity and the structure of crystals, though it has not yet been proved that optical activity is entirely produced by the peculiar struc-

ture of such crystals. The fact, pointed out by Groth, that some substances only rotate the plane of polarisation when in the solid form, is not a complete proof, as on entering into solution equivalent amounts of laevo- and dextro-rotatory substances may be formed and so make the solution inactive. As a matter of fact, Groth has found that a solution of $NaClO_3$ in which laevo- and dextro-rotatory crystals of this substance are dissolved, can deposit both laevo- and dextro-rotatory crystals.

If the optical activity is entirely conditioned by the peculiar crystalline form of some substances, enantiomorphous crystals, such as the regular tetrahedric or trapezoidal hemihedric substances, should necessarily have the power of circular polarisation. This is not the case. For instance, L. Wulff[691] has shown that lead, barium and strontium nitrates, in spite of the regular tetrahedric form of their crystals, i.e. their enantiomorphous constitution, have no effect on the plane of polarisation either in the solid or dissolved state. A further series of substances whose crystalline form is that of the trapezoidal hemihedric substances did not show any optical activity when examined by Wulff. This fact implies that the cause of the property of circular polarisation must be dependent on the chemical constitution of the crystal nuclei, quite apart from the physical structure of the crystal; optically active substances must not only be enantiomorphous, but must have a definite chemical structure. For instance, lead, barium and strontium nitrates are truly enantiomorphous, but they do not possess the structure of optically active substances and they are, therefore, optically inactive. Hence it is necessary to enquire what chemical structure is essential to render enantiomorphous substances optically active.

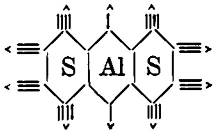
It is probable that the optical anomalies of some regularly crystallisable substances are of a constitutional nature, and if the chemical factors, such as those which cause the optical abnormalities of the alums, could be discovered, it is not improbable that these factors would be the causes of circular polarisation.

The following facts show that chemical structure has an undoubted influence on the optical properties of crystals :

Mallard, in his studies of the zeolites, has observed that, on prolonged heating, these slowly change their optical properties in consequence of the steady loss of their water of crystallisation, i.e. by changes in the side-chains, until finally the crystal has the properties of the anhydrous substance. This condition continues if a re-absorption of water is prevented, as by embedding in Canada balsam; but if the temperature reached has not been excessive and the crystal is allowed to cool in moist air it will regain its water almost completely, and, simultaneously with this, its optical properties. In this way Mallard has found a direct proof for the dependence of the optical characters on the chemical constitution.

In the case of circularising substances, it is noteworthy that Le

Bel[692] and van't Hoff[693] discovered, almost simultaneously, the fact that all organic compounds which rotate the plane of polarisation of light contain asymmetric carbon atoms, i.e. carbon atoms in which each of the four valencies is saturated with a different group of atoms. As it has been observed that all organic substances which are optically active contain one or more asymmetric carbon atoms, it appears probable that the source of optical anomalies and of circular polarisation may be due to this asymmetry or to an asymmetrical substitution of the side-chains or of the hexite and pentite in some substances. From this it follows that a potash alum of the structural formula

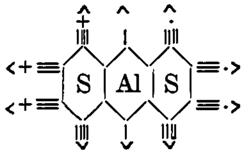


$$3\,K_2O \cdot 12\,H_2O \cdot 3\,Al_2O_3 \cdot 12\,SO_3 \cdot 10\,\hat{H}$$

will have a normal optical behaviour, i.e. it must be isotropic. If, however, part of the potassium is replaced by sodium, lithium or a similar metal, or if part of the aluminium is replaced by Fe''', Cr''', Mn''', etc., or if part of the sulphur is replaced asymmetrically by selenium, the crystalline form remaining unchanged, i.e. regular, these substances will be optically anisotropic.

In an analogous manner the source of circular polarisation may be considered as due to the chemical structure of enantiomorphous substances.

It is not surprising that Brauns[694] has shown experimentally that, as a matter of fact, the pure alums are optically isotropic, but the mixed ones are double refracting, i.e. anisotropic. According to Brauns, all crystals of pure potash-alumina-alum and ammonia-alumina-alum are optically isotropic, but those crystals which are produced from solutions of the mixed substances are optically different and show a double refraction. Crystals obtained from a solution containing equal weights of ammonia- and potash-alum show, according to Brauns, a very strong double refraction, are full of irregular cracks, and, on removing them from the solution, they fall to pieces. On representing the structure of such an alum by



the NH_4-groups being marked + and the potassium atoms · its asymmetric structure is clear and the abnormal optical behaviour of this alum, the irregular cracks in it, and the falling to pieces of the crystals on removing them from the solution are rendered explicable.

It is noteworthy that Brauns has observed faint circular polarisation phenomena, in consequence of which it is highly probable that such asymmetric substitution is the cause of the optical activity of a number of enantiomorphous substances. As a matter of fact, the micas from which Reusch built his optically active compounds are silicates in which both the side-chains and the aluminium hexites and pentites are composed of different constituents which are often asymmetrically arranged in the molecule (see "Micas" in *Appendix*).

Some substances, such as quartz, are optically active and, without exception, possess enantiomorphous crystalline forms. Their structural formulæ, as derived from ultimate analyses and other studies, must be asymmetric if this theory of circular polarisation is correct and of general application.

The Bravais-Frankenheim theory of crystalline structure does not indicate the enantiomorphous forms. Sohncke sought for the source of optical rotation of some crystals and of the appearance of these in enantiomorphous forms in an inner structure of the same, which is similar to Reusch's mica arrangement. The theory of crystalline structure may be enlarged in this direction. The optically active crystals consist, according to him, of step-like lamellæ which are optically bi-axial and do not show double refraction in the axis of rotation, but show circular polarisation effects.

The S.H.P. theory may also be enlarged in the same sense. The units may be so arranged that a series of double pyramids (see P and P′, pp. 286 and 287) P, P′, P″, P‴ . . . with the surfaces ABDE, A′B′D′E′, A″B″D″E″ . . . are produced. These double pyramids P, P′, P″ . . . have axes AD, A′D′, A″D″ . . . BE, B′E′, B″E″ . . . and are so placed that each of their axes in the base forms an angle of 120° in the direction of the movement of the hands of a clock, or *vice versâ* with the corresponding axes of the next base, i.e. AD with A′D′, A′D′ with A″D″, A″D″ with A‴D‴. In the first case dextro-, and in the second laevo-rotatory crystals are produced, provided that the crystals are also chemically asymmetric.

The S.H.P. theory thus provides a single explanation for the cause of circular polarisation in both organic and inorganic compounds.

E. The Dependence of the Geometrical Constants on the Temperature

The bonds between the nuclei of the radicles (i.e. the hexites and pentites) and between the radicles and the side-chains are loosened by the addition of bases, water of constitution and of crystallisation and on raising the temperature. Hence, on altering the temperature the geometric constants must be influenced, as they have a close relationship to the valency-forces. The consequence of the theory is also confirmed by the facts.

Mitscherlich[695], G. Rose[696], F. de Filippi[697], Frankenheim[698] and others have shown that when aragonite is heated to a suitable

temperature it is converted into calcspar. Hauy[699] has also observed that on heating aragonite to a dull red heat it falls to powder, and Haidinger[700] represented this process as a conversion of aragonite into calcspar. G. Rose[701] has shown that calcite and also aragonite are formed from warm solutions of $CaCO_3$ and that, at higher temperatures, only calcite is formed. C. Klein[702] has made the interesting observation that a plate cut from aragonite in a direction vertical to the principal axis becomes optically monoaxial and has a negative double refraction when heated, i.e. the plate assumes the characteristic properties of calcspar when warmed.

The changes of the crystalline forms of substances on raising their temperature has been observed in numerous cases by O. Lehmann[703], who has examined two groups of polymerised substances, of which:

1. The members of one group are converted, with absorption of heat, into another modification; on cooling, the original form (enantiotropic modification) is reproduced and heat is evolved.
2. The members of the other group are stable and labile modifications which differ from the enantiotropic substances and are not converted into other forms on alteration of the temperature.

F. Molecular Volumes and the S.H.P. Theory

It follows from the S.H.P. theory that the molecular volumes of analogously constituted substances cannot be identical, as the affinities between the various nuclei must differ from each other.

An interesting confirmation of this consequence of the theory is found in the results of investigations of the molecular volumes of a series of alums by O. Petterson[704], which are shown in the following Table:

Sulphate Alums	Mol. Vols.	Selenate Alums	Mol. Vols.	Differ. between Vols.
$\check{K}_6H^0_{24}(\hat{S}\cdot\hat{Al}\cdot\hat{S}.)\cdot 10\,\hat{H}$	541.6	$K^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	568.0	26.4
$(NH_4)^0_6H^0_{24}(\hat{S}\cdot\hat{Al}\cdot\hat{S})\cdot 10\,\hat{H}$	552.2	$(NH_4)^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	578.6	26.4
$Rb^0_6H^0_{24}(\hat{S}\cdot\hat{Al}\cdot\hat{S})\cdot 10\,\hat{H}$	551.0	$Rb^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	576.2	25.2
$Cs^0_6H^0_{24}(\hat{S}\cdot\hat{Al}\cdot\hat{S})\cdot 10\,\hat{H}$	569.2	$Cs^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	595.6	26.4
$K^0_6H^0_{24}(\hat{S}\cdot\hat{Cr}\cdot\hat{S})\cdot 10\,\hat{H}$	542.2	$K^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	571.0	28.8
$(NH_4)^0_6H^0_{24}(\hat{S}\cdot\hat{Cr}\cdot\hat{S})\cdot 10\,\hat{H}$	553.6	$(NH_4)^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	577.4	23.8
$Rb^0_6H^0_{24}(\hat{S}\cdot\hat{Cr}\cdot\hat{S})\cdot 10\,\hat{H}$	554.6	$Rb^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	576.8	22.2
$Tl^0_6H^0_{24}(\hat{S}\cdot\hat{Cr}\cdot\hat{S})\cdot 10\,\hat{H}$	554.2	$Tl^0_6H^0_{24}(\hat{Se}\cdot\hat{Al}\cdot\hat{Se})\cdot 10\,\hat{H}$	576.6	22.4

From this Table it may be seen that not only are the molecular volumes of different alums not identical, but that there is a striking regularity in the difference in the molecular volumes caused by the substitution of selenium for sulphur.

Summary and Conclusions

IN the foregoing pages an attempt has been made to obtain a glance at the structure of the silicon compounds. After a critical examination of existing theories which have been proposed for the representation of the structure of the aluminosilicates and the silicates generally, it has been found that the conception of the aluminosilicates as complex acids or salts of complex acids agrees best with the facts. The reactions of the aluminosilicates can only be understood if both alumina and silica are regarded as playing similar rôles in the silicates, i.e. the rôles of acids. A number of properties appear, however, to contradict the theory of the aluminosilicates as complex compounds, and this conception does not enable any systematic arrangement to be made of all the aluminosilicates in spite of the undoubted genetic relationship between them.

It is very surprising that scarcely any of the critics of the German edition of this work have paid any attention to the main thesis that the silicates, or more correctly the aluminosilicates, should be classed with the complex acids. Yet it is stated quite definitely on page 30: "It is, however, not improbable that these objections (i.e. to the sixth hypothesis) are only *apparent*, and that they would be completely overcome if the manner in which the atoms in the anhydrides of the aluminosilicates are bound to each other were known. By the use of a suitable hypothesis for the structure of these anhydrides a confirmation of this statement may be found. The authors of this present volume have actually formulated such a hypothesis, and its nature and the conclusions to be drawn from it form the subject-matter of the following pages."

On page 62 it is stated that: "The conclusion has already (see pp. 22 and 26) been reached that, of all the theories devised for showing the constitution of the aluminosilicates, the one which agrees best with the facts is that which assumes that these compounds are complex acids and the corresponding salts."

On page 63 it is stated that: "The conception of the aluminosilicates as complex acids thus agrees excellently with the experimental results."

On pages 79–102 it is shown that the molybdenum and tungsten complexes, i.e. the complex acids and their salts, are *par excellence* true analogues of the aluminosilicates and agree perfectly with structural formulæ which are fully analogous to those used for the aluminosilicates.

The foregoing quotations, and the present work as a whole, show clearly that, quite apart from the hexite-pentite theory, the view that aluminosilicates are complex acids and salts is the foundation on which a knowledge of the constitution of these substances must be based. Yet this fact, as already remarked, does not appear to have been noticed by a single critic. Thus, in a review by J. J. P.[766] it is stated that: "The conception of hexite and pentite radicles (ring-compounds with 5 or 6 Al- or Si-atoms and a number of O-atoms) is the foundation of a systematic study of the silicates."

Stremme[767] commences with the view that the hexite-pentite theory is the sole foundation of the present volume, and then reaches the remarkable conclusion that the chief difficulty in mineral chemistry —the explanation of the extraordinarily great variations in the composition of the silicates—becomes "playfully easy," "it is only necessary to introduce new hexite and pentite groups into existing combinations." He then stated that: "In not a single case is it shown that even one silicate must necessarily contain a hexite or pentite group."

In reply to this criticism, which completely overlooks the complex nature of the aluminosilicates, it may be well to remark that the H.P. structural formulæ of the aluminosilicates have been devised in accordance with definite rules, and in no case have "new hexites or pentites" been introduced in a haphazard manner. The proof that the aluminosilicates have the constitution indicated by the H.P. theory (i.e. that they contain hexites or pentites of silicon and aluminium which are arranged in accordance with definite laws) has been published in the customary scientific manner, as everyone who will read it impartially must admit. The theoretically possible formulæ were first set down, and the consequences deducible from them were then compared with the available experimental evidence. Stremme terms this "not proved," and his contention might be sound if the experimental evidence did not agree with the logical conclusions from the theory. As a matter of fact, the agreement is remarkably close. If Stremme or any other critic can find a better method of testing a theory than the one adopted in the present volume, he would render an inestimable service to mankind if he would publish it.

The method adopted by this critic to show the "worthlessness" of the H.P. theory could be easily used to upset the most firmly-established theories. For example, on what foundations are the atomic theory, the benzene theory and the theory of dissociation based? Surely they have been accepted as the result of entirely analogous methods of argument to those used in the present volume!

C. H. Desch[736] has overlooked the fact that the main foundation of this exposition of the constitution of aluminosilicates is the fact of their complex nature, inasmuch as he states that "the felspars, the hardening of cements, the hydration of zeolites . . . are dealt with exclusively from a structural chemical point of view."

A further criticism of Desch's views will be found on reference to the Name Index.

Allen and Shepherd[737] also appear to have completely overlooked the fact that the complex nature of the aluminosilicates is the essential basis of the constitution attributed to them by the authors of the H.P. theory, and it appears strange to them that the structure of the complex compounds of tungsten, vanadium and molybdenum should also be described in the present volume. It is, nevertheless, very remarkable that Allen and Shepherd have overlooked this fact, or even that they could overlook it, as they specifically refer to "an excellent review of previous theories of the structure of silicates and a proof of their insufficiency" contained in the present work. Yet in this review it is clearly shown that the starting point of any theory of aluminosilicates must be based on their complex nature. It is the neglect of this which leads Allen and Shepherd to oppose the application of the new theory to Portland cements. If they had only seen that the aluminosilicates are complex acids or the corresponding salts, they must have realised the *a priori* probability of the existence of highly basic calcium aluminosilicates, i.e. they must have reached a conception of the constitution of Portland cements which agrees with the one herein published. If a theory shows the possible existence of these substances, and all their properties agree with the structural formulæ which are based on the theory, there is no reason to doubt the correctness of the constitutions thus formulated.

Manchot[775], alone of all the critics, refers to the complex nature of the aluminosilicates. From his statement—"It is in any case worth consideration whether it can be proved that among the silicates as in other branches of chemistry the number 6 plays so special a part"—it follows that he considers that the new theory cannot in any way be regarded as properly supported by facts. This critic should, however, state, at the earliest opportunity, how large must be the mass of facts in support of a theory before he would consider that theory established. If his attitude in his own researches may be regarded as satisfactory to himself, he will doubtless be interested to refer to an investigation he made in 1905 into the constitution of silicides and published in the "Annalen der Chemie," 1905, *342*, 356–363. In this instance this investigator did not hesitate to state that these compounds form hexites, notwithstanding that he had *only a single fact* upon which to rely for his conclusion, viz. the behaviour of these substances towards hydrofluoric acid. Yet when he comes to review the German edition of the present work, he considers that the innumerable facts and the whole mass of available experimental evidence are not sufficient to establish the hexite formation of the silicates! The number and importance of these facts and the manner in which this critic uses his own experimental results in criticising the constitutional formulæ of the silicates—quietly passing over in silence those which may happen to agree with the theory he is criticising—is highly significant (see p. 273).

The H.P. theory is the first one enabling structural formulæ to be devised in agreement with the conception of the aluminosilicates as complex compounds, which is free from the drawbacks of the earlier theories, is capable of being used in the systematic arrangement of all the silicates and also enables a series of properties of the aluminosilicates to be predicted *a priori*, which have, so far as they have been investigated experimentally, been fully confirmed.

Thus the structural formulæ of the silicates devised by means of the H.P. theory have led to the remarkable prediction that all the aluminium and silicon atoms in the aluminosilicates will not behave exactly alike when examined chemically and physio-chemically, and that atoms occupying certain positions in the molecule will behave differently from the rest. This consequence of the theory is fully confirmed by the available experimental material, and particularly by the work of Thugutt, Silber and others.

The agreement between the minimum molecular weights which may be inferred from the H.P. theory and those found experimentally is also important, particularly as regards the results obtained by Thugutt on a series of aluminosilicates such as orthoclase, nepheline, and the sodalites.

Considerable importance also attaches to that consequence of the H.P. theory which states that chemical compounds may contain various kinds of combined water—" water of constitution " and " water of crystallisation "—the first being acid-water and the second basic-water, and to the agreement of this consequence with the facts ascertained experimentally—such as Clarke's studies of the zeolites.

The H.P. theory is not only applicable to the representation of the structure of the aluminosilicates, but to the complex acids generally. According to the investigations of Gibbs, Blomstrand, Péchard, Parmentier, Kehrmann, Friedheim and others, complex acids are produced by the union of one acid with another, e.g. of molybdic acid with vanadic, phosphoric, antimonic or arsenic acid; and of aluminic acid with phosphoric, vanadic, molybdic, sulphuric or tungstic acid. By means of the H.P. theory the structure of all the various complex acids and their salts can be shown on *a priori* grounds. This theory also shows that a genetic relationship must exist between the various complex acids of the same class, e.g. between all the aluminosilicates, all the aluminophosphates, all the aluminosulphates, and between all the salts of the complex acids of the same class. As a matter of fact, such a relationship does exist, as may be seen on examination of the available experimental results.

It is specially important to observe the fact that the addition of a basic or other side-chain weakens the bonds of the nucleus, and that the most stable types of the complex acids are those in which the ratio of the acid-forming atoms is 1 : 1 ; thus, the most stable aluminosilicates

are those with a ratio of Al_2O_3 : SiO_2=1 : 2; the most stable vanadotungstates are those in which V_2O_5 : WO_3=1 : 2.

The H.P. theory is also of value in ascertaining the constitution of several aluminosilicates of great technical importance, such as clays, ultramarines, Portland cements, slag cements, porcelain cements, etc. The clays are of great technical value because they are a raw material used in the production of pottery, cement, ultramarines, etc., and they are also of great theoretical importance because they constitute some of the various aluminosilicic acids whose existence may be inferred from the H.P. theory. The behaviour of clays towards strong acids (the so-called "rational analysis"), the cause of the plasticity of clays and the changes which occur on burning may all be explained by means of the H.P. theory. Innumerable investigations have been made in order to ascertain the constitution of the ultramarines. The H.P. theory supplies a hypothesis from which the structure of the whole of the theoretically possible substances of the ultramarine class may be derived; a large number of these compounds are already known to exist. On the other hand, no ultramarines have yet been found which, according to the theory, are theoretically impossible (such as those in which Al_2O_3 : SiO_2=1 : 6). The ultramarine theory, based on the more general H.P. theory, is in entire agreement with the experimental results of the valuable work of Hoffmann, Heumann, Philipp, Szilasi, Gmelin and others. The experimental work of Guckelberger on the minimum molecular weight of some ultramarines is in remarkable agreement with the H.P. theory and is fully confirmatory of the theoretical inferences from it.

Innumerable attempts have also been made to ascertain the structure of Portland, slag, porcelain and other silicate cements and especially to explain the reactions which occur during the hardening of these cements. These and other problems find a clear and simple solution when once the structure of the silicates has been ascertained by means of a suitable theory. As a matter of fact, the H.P. theory has led to conceptions of the structure of cements which not only agree with experimental observations, but also permit of very full prognostications in regard to the possibility of solving the great problem of the use of cement in sea-water and coastal masonry.

The new H.P. theory has proved to be of special value in ascertaining the structure of the porcelain (dental) cements, i.e. those compounds which are both theoretically and practically important on account of their extended use in dentistry.

The poisonous action of some of these cements has been studied, and the H.P. theory shows which portion of these cements has a toxic action and it indicates how their poisonous nature may be destroyed and the cements rendered quite harmless. To solve this obviously physiological chemical problem it is necessary to study the toxines generally in order to ascertain the nature of their actions and the

causes of the poisoning. Ehrlich's theory of the toxines on the one hand and the H.P. theory on the other combine to solve the problem of the poisonous nature of many porcelain cements and show clearly which of the available cements are toxic, or at least risky, and which are harmless.

The aluminosilicates, generally speaking, cannot be satisfactorily studied because of their great resistance to reagents, few of the ordinary methods of investigation being available. Yet, by means of the H.P. theory, it is possible to produce a theory of such general application that, with the aid of modern methods of investigation, the constitution of all the silicates may be ascertained. For instance, the results of physical and chemical researches on the silico-molybdates by W. Asch are in complete agreement with the H.P. theory. This agreement between the facts and theory is very striking in the case of the alums and chromo-sulphuric acids which have been specially studied in a chemico-physical manner by Recoura and Whitney.

There can be no doubt that Nature has formed all substances according to monistic laws. Hence the probability of the H.P. theory being extended so as to make it applicable as a general chemical theory.

An attempt thus to enlarge the scope of the H.P. theory, though made on only a small scale, has led to a new theory of acids, new views on the constitution of solutions and new views of the structure of carbon compounds.

The H.P. theory itself does not take cognisance of the fact that atoms exist in space; consequently it required extension and combination with the modern theory of the structure of crystals in order to convert it into a general stereo-chemical theory. This has been accomplished to the extent that, by means of the "hexite-pentite law" (p. 289), the stereo-hexite-pentite theory (abbreviated to "S.H.P." theory) is capable of development into a general theory of chemical compounds. The S.H.P. theory has proved to be of great value; it helps to explain many puzzling properties of crystals, confirms Hauy's law of relationship between crystalline form and chemical composition, permits the prediction of isomers of chemically allied substances (Mitscherlich) and solves the problem of the structure of the so-called isomorphous mixtures. Thus, the H.P. theory may be compared to a bridge between the realms of organic and inorganic chemistry, and the S.H.P. theory to an indivisible bond between chemistry and the allied sciences of physics and crystallography.

The S.H.P. theory appears to be particularly valuable when it is compared with existing theories of the constitution of chemical compounds. It is then seen that many modern theories are, in a sense, only portions of the new theory and may be inferred from it.

In a review of the German edition of the present work by Stremme[767]

the following remark occurs: "In short, an attempt is made to develop a Chemistry of Silicon corresponding to that of Carbon such as has so frequently been attempted by others." As a matter of fact, the view that Nature forms substances in accordance with monistic laws, permits many applications of the results of the study of organic compounds (including their structural formulæ) to inorganic substances. The critic must therefore ascertain what beneficial results (if any) have resulted from the present investigation and whether previous investigations are completely analogous to it. He is compelled to deny the analogy if he compares the results of this investigation with previous ones. In order to show this more clearly, two investigations of the relationship between the compounds of silicon and carbon, both of great importance to a study of the structure of silicates, may here be critically examined, viz. that of A. Ŝafařik[768] and that of W. Vernadsky[769].

A. Ŝafařik has endeavoured to find a complete analogy between silicates and organic compounds and has assumed that the silicates are open or closed ring-compounds such as are found in the aliphatic and aromatic compounds of carbon. This analogy between silicon and carbon, the former being a constituent of the inorganic crust of the earth and the latter the foundation of all organic nature, "thus assumes a new and deeper significance." In addition to this analogy there is, according to Ŝafařik, a difference between the compounds of silicon and carbon inasmuch as in the silicates silicon is bound to silicon through oxygen and the polyvalent metals, whilst in the organic compounds there is a direct bond between carbon and carbon.

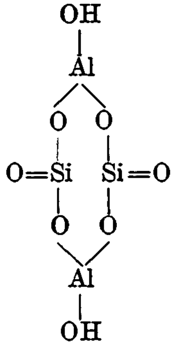
A glance at Ŝafařik's formula shows at once that it differs greatly from those derived from the H.P. theory. The necessary explanatory support is lacking for Ŝafařik's theory of the silicates, and for this reason it cannot be applied to the silicates as a whole. An important disadvantage of his structural formula is due to the fact that it is not based on any natural law and that it contains a dualism, the origin of which may be found in the present dualistic conception of organic chemistry, viz. the division of organic compounds into an aliphatic and an aromatic series. The result is that this theory, notwithstanding its derivation from organic chemistry, has not led Ŝafařik very far. The poor result which he has obtained in applying organic theories to inorganic compounds caused Ŝafařik to make the following remarks: "The most natural means of bringing inorganic chemistry into unison with the fundamental theories of the present time is that which has led to such remarkably successful results in organic chemistry; each single element must be examined in such a manner as has been the case with carbon or, as Erlenmeyer so pregnantly observed, we must have as many chemistries as there

are elements. To attempt this work would be to commence a task of incredible magnitude."

From these words it is clear how little satisfaction Šafařik obtained from his researches, and the authors of the present volume are equally unable to accept the view that the problems of the structure of chemical compounds can ever be solved by simply studying the elements in a systematic manner. They incline more to the opinion that if the present conception of the structure of organic compounds cannot be applied to inorganic substances, then this very inapplicability is the best proof that the generally accepted theory of organic structures is not so devoid of objection that it cannot, with advantage, be modified. The possibility or otherwise of applying a theory which appears to be satisfactory for one element to others is one of the best tests of the value of such a theory.

W. Vernadsky has also endeavoured to devise structural formulæ for silicates which bear some resemblance to those of organic chemistry. He assumed the existence of two radicles in aluminosilicates: one with an open or chlorite ring and the other with a closed or cyclic chain (mica ring). The constitution of these rings is shown by the following formulæ :

Chlorite Ring.



Mica Ring.

According to Vernadsky these rings remain unaltered in most chemical reactions, this property being highly characteristic of the aluminosilicates. The compounds with a mica ring are, according to this investigator, much more strongly characterised than minerals with a chlorite ring.

As the durability of the rings is characteristic of cyclic chemical compounds, and experience in organic chemistry shows that this durability is exceptionally high in heterocyclic compounds, Vernadsky considered that it might be assumed that minerals containing mica contain heterocyclic rings, i.e. rings composed of several elements.

Vernadsky has had no specially satisfactory results from this

theory because, as he himself admits, it is necessary to limit the application of the theory to the simplest and best known compounds, and because he persistently adheres to an entirely unnecessary dualism, inasmuch as he divides silicates into two groups: one containing those which are undoubtedly chemical compounds and the other comprising the so-called physical combinations. Vernadsky's theory is thus inapplicable as a general theory of silicates and also as a monistic chemical theory of general application.

This short statement with regard to important attempts to apply the theories current in organic chemistry to the elucidation of inorganic structures must suffice to show that there is no parallel between such an application of existing theories and the H.P. theory developed in the present volume. Hence, before the H.P. theory can be discarded or regarded as of no importance, those who criticise it must disprove the statements made and must show that a still larger number of facts can be fairly used in support of a new theory which, so far as those concerned with the writing and translation of the present volume are aware, has not yet been published. The ineffectiveness of all the noteworthy existing theories has, it is believed, been conclusively shown in the foregoing pages.

The H.P. theory leads—by quite different means from those hitherto used—to the "benzene-ring theory" which has proved so advantageous in studying the constitution and properties of carbon compounds. It is scarcely necessary to state that Werner's *co-ordination law* is, in some respects, a part of the S.H.P. theory. If $a=b=c=1$ and $\alpha=\beta=\gamma=90°$, this produces Werner's octohedron, to the corners of which are attached the molecules of various metal ammonias and allied substances. It is a strong confirmation of the S.H.P. theory that Werner's co-ordination law has solved a number of puzzling problems in connection with the metal ammonias and allied substances, that its inferences have been fully confirmed by experiment, and that Werner's theory has proved of value in the development of a systematic arrangement of the compounds concerned.

Arrhenius' "Dissociation Hypothesis," van't Hoff's "Theory of Solutions," and the Kinetic Theory of Gases are all, in a certain sense, capable of being regarded as consequences of the S.H.P. theory.

It is particularly important to note that, by the combination of the S.H.P. theory with the modern theory of the structure of crystals, a great step towards the object of all investigation has been made, and some approach has been effected to the time when it will be possible to show the true relationship between crystalline form and chemical composition. This object will, clearly, be attained as soon as it is possible to ascertain the exact relationship between the geometrical constants ($a:b:c$ and α, β and γ) and the chemical constants, and to predict both from the structural formula.

De Bois-Reymond[705] has no doubt that these problems will be

solved as soon as structural chemistry and crystallography unite, and he has written the following: "We see, in imagination, Structural Chemistry reaching out her hand to Crystallography; we see the atoms with their measured valencies filling spaces of definite shapes, and forming the tools employed in building crystals."

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APPENDIX

CALCULATION OF FORMULÆ FROM THE RESULTS OF LEMBERG'S EXPERIMENTS *

A. Production of a series of Sodalites with the general formula

$$m\,Na_2O \cdot (6\,Al_2O_3 \cdot 12\,SiO_2) \cdot m'\,\text{Salt} \cdot n\,H_2O$$

or the formula

$$\overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot m'\Sigma \cdot n\,H^2O$$

(a) The following compound

$$(6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 4\,NaCl \cdot 4\,H_2O$$
$$= \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 4\,NaCl \cdot 4\,H_2O$$

is the final product of the action of a 20 per cent. solution of caustic soda saturated with sodium chloride on the following silicates:

$6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O$ (Kaolin from Karlsbad)
$= H_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O$

$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2$ (Eläolite from Brevig)
$= \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 12\,H_2O$ (Brevicite from Brevig)
$= \overset{\circ}{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 12\,H_2O$

$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O$ (Analcime from Fassthal)
$= \overset{\circ}{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\,H_2O$

$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (Leucite from Vesuvius)
$= \overset{\circ}{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$

$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$ (Orthoclase from Striegau)

$$= \overset{\circ}{K}_6\left(\hat{Al}\begin{cases}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{cases}\right)$$

the reagent and silicate being treated at various temperatures (100°, 180 to 190° C.) for various periods ranging from 74 hours to six months.

	Theory.	4	4f	4g	4c	4d	4a
$3\,Na_2O$	18.51	19.02	18.65	19.35	19.04	18.53	18.57
$3\,Al_2O_3$	30.45	31.63	31.81	31.61	30.70	30.84	30.73
$6\,SiO_2$	35.82	35.14	36.32	36.66	36.02	36.42	36.78
2 NaCl	11.64	10.71	11.22	11.32	10.22	10.22	10.23
$2\,H_2O$	3.58	2.61	0.94	1.14	3.60	3.13	3.25
CaO	—	0.30	0.63	—	0.14	0.49	0.25
	100.00	99.41	99.57	100.08	99.72	99.63	99.81

* [1] Zeitschr. d. Deutsch. geol. Gesellsch. 1876–85.
[2] Cf. pages 60, 61 and 140 of this volume.
[3] Cf. Lemberg, *l.* c. 1883, p. 582.

(b) After two months' action, at 100°, of 15 and 12 per cent. solutions of caustic potash saturated with potassium chloride on the silicates *

$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (Leucite from Vesuvius) $= \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$

$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$ (Orthoclase from Striegau) $= \mathring{K}_6\left(\hat{Al}\begin{matrix} \diagup \hat{Si} \\ - \hat{Si} \\ \diagdown \hat{Si} \end{matrix}\right)$

Lemberg obtained the sodalite

$$(6\,K_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 2\,KCl \cdot 8\,H_2O$$
$$= \mathring{K}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot Si) \cdot 2\,KCl \cdot 8\,H_2O.$$

	Theory.	6c	6a
$3\,K_2O$	25.77	24.72	23.84
$3\,Al_2O_3$	27.96	27.47	27.10
$6\,SiO_2$	32.89	32.31	32.26
KCl	6.80	7.34	7.00
$4\,H_2O$	6.58	7.80	8.22
CaO	—	0.30	—
	100.00	99.94	99.42

(c) The silicates †

$6\,H_2O \cdot 6\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O$ (Kaolin from Karlsbad)
$= \mathring{H}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})\,6\,H_2O$

$6\,Na_2O \cdot 6\,Al_2O_3 \cdot 18\,SiO_2 \cdot 12\,H_2O$ (Brevicite from Brevig)
$= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si})\,12\,H_2O$

$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2 \cdot 6\,H_2O$ (Analcime from Fassthal)
$= \mathring{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})\,6\,H_2O$

$3\,K_2O \cdot 3\,Al_2O_3 \cdot 12\,SiO_2$ (Leucite from Vesuvius)
$= \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$

$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$ (Albite from Viesch)

$$= \mathring{Na}_6\left(\hat{Al}\begin{matrix} \diagup \hat{Si} \\ - \hat{Si} \\ \diagdown \hat{Si} \end{matrix}\right)$$

$3\,K_2O \cdot 3\,Al_2O_3 \cdot 18\,SiO_2$ (Orthoclase from Striegau)

$$= \mathring{K}_6\left(\hat{Al}\begin{matrix} \diagup \hat{Si} \\ - \hat{Si} \\ \diagdown \hat{Si} \end{matrix}\right)$$

* Lemberg, *l. c.* 1883, p. 587.
† Lemberg, *l. c.* 1883, pp. 579, 580.

If a 20 per cent. solution of caustic soda, saturated with sodium sulphate, is used at various temperatures (100°, 180-190°) for different periods (74 hours to six months) only the following sodalite is formed :

$$(6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_2SO_4 \cdot 6\ H_2O$$
$$= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 2\ Na_2SO_4 \cdot 6\ H_2O.$$

	Theory.	3	3f	3a	3b	38	3c	3d
3 Na_2O	17.75	17.96	17.75	17.72	17.77	17.39	17.11	18.53
3 Al_2O_3	29.20	30.00	30.24	29.44	29.55	29.66	29.01	30.04
6 SiO_2	34.35	34.31	34.03	14.78	34.29	35.14	35.27	34.74
Na_2SO_4	13.55	11.82	13.22	12.65	11.80	12.63	11.21	9.33
3 H_2O	5.15	5.70	5.02	5.35	5.89	4.90	6.25	5.88
CaO	—	0.35	—	—	0.40	—	0.20	0.20
	100.00	100.14	100.26	99.94	99.70	99.72	99.05	98.72

(d) Three to five grammes of the following silicates : *

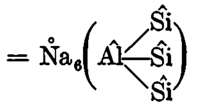
$6\ H_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O$ (Kaolin from Karlsbad)
$= \mathring{H}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O$

$6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2$ (Eläolite from Brevig)
$= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})$

$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O$ (Analcime from Fassthal)
$= \mathring{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O$

$3\ K_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2$ (Leucite from Vesuvius)
$= \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$

$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2$ (Albite from Viesch)



were mixed with 40 g. of the sodium silicate $Na_2O \cdot SiO_2 \cdot 8\ H_2O$, which had been melted in its own water of crystallisation and the mixture heated at 200° for 100 hours in a digester. The excess of sodium silicate was then washed out with cold water. An analysis of the residue corresponded to the compound

$$(6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 2\ Na_2SiO_3 \cdot 8\ H_2O$$
$$= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 2\ Na_2SiO_3 \cdot 8\ H_2O.$$

	Theory.	3	3c	3e	3f	3g
4 Na_2O	23.71	22.61	23.30	23.34	21.03	21.70
3 Al_2O_3	29.27	29.31	28.69	29.16	29.60	29.25
7 SiO_2	40.15	40.30	39.43	40.15	40.52	40.84
4 H_2O	6.87	6.68	6.88	6.38	7.49	6.94
CaO	—	—	0.90	—	—	—
	100.00	98.90	99.20	99.03	98.64	99.73

* Lemberg, *l.* c. 1885, pp. 961, 962.

(e) The silicates

$$6\ H_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O \text{ (Kaolin from Karlsbad)}$$
$$= \mathring{H}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O$$
$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O \text{ (Analcime from Fassthal)}$$
$$= \mathring{Na}_6 \cdot (\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O$$
$$3\ K_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \text{ (Leucite from Vesuvius)}$$
$$= \mathring{K}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si})$$

were treated with a 15-20 per cent. solution of caustic soda saturated with sodium carbonate at various temperatures (100°, 180–190°) and for different periods ranging from 74 hours to six months.* Analyses of the products gave the following formula:

$$3\ (6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 4\ Na_2CO_3 \cdot 30\ H_2O$$
$$= \{\mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})\}_3 \cdot 4\ Na_2CO_3 \cdot 30\ H_2O.$$

	Theory.	5	5b	5c
9 Na_2O	18.38	18.23	17.17	18.13
9 Al_2O_2	30.22	30.84	29.18	29.47
18 SiO_2	35.55	34.82	35.50	35.27
2 Na_2OC_3	6.96	7.13	6.96	6.58
15 H_2O	8.89	8.68	9.40	9.18
CaO	—	0.30	0.10	0.40
	100.00	100.00	98.84	99.03

B. A Series of Changes in Aluminosilicates based on Lemberg's Experiments.

(a) The action of caustic soda solution of various concentrations (30 per cent. and 56 per cent.) at 100° for various periods ranging from 72 hours to 14 days on the following silicates:

(1) $3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O$ (Analcime from Fassthal)
$$= \mathring{Na}_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O†$$
(2) $6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2$ (Eläolite from Brevig)
$$= \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})‡$$
(3) $6\ H_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O$ (Kaolin from Karlsbad)
$$= \mathring{H}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O§$$

gave the following results:

From Compound 1 was obtained the substance:

$$6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 15\ H_2O = \mathring{Na}_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 15\ H_2O$$

from Compound 2 the substance:

$$8\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 7\ H_2O = \mathring{Na}_{16}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 7\ H_2O$$

* Lemberg, *l.* c. 1883, pp. 583–4.
† Lemberg, *l.* c. 1883, p. 579, Expt. 2.
‡ Lemberg, *l.* c. 1885, pp. 960–1, Expts. 2c. and 2d.
§ Lemberg, *l.* c. 1883, p. 579, Expt. 1; *l. c.* 1885, p. 960, Expt. 2b.

and from Compound 3 the silicates:

$$6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 15\ H_2O = \mathring{N}a_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 15\ H_2O$$
$$8\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2 \cdot 7\ H_2O = \mathring{N}a_{16}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si}) \cdot 7\ H_2O$$

	Theory.	1	2
6 Na_2O	18.84	18.30	18.87
6 Al_2O_3	31.01	31.13	31.35
12 SiO_2	36.47	36.52	36.28
15 H_2O	13.68	14.59	13.39
	100.00	100.54	99.89

	Theory.	2b	2c	2d
8 Na_2O	25.38	26.05	25.29	24.99
6 Al_2O_3	31.32	31.42	31.05	31.16
12 SiO_2	36.85	36.25	36.63	36.12
7 H_2O	6.45	6.87	5.71	6.36
CaO	—	—	1.08	1.02
	100.00	100.59	99.76	99.65

(b) On treating the silicates:

(1) $6\ Na_2O \cdot 6\ Al_2O_3 \cdot 12\ SiO_2$ (Eläolite from Brevig)
$$= \mathring{N}a_{12}(\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si})^{*}$$

(2) $3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O$ (Analcime from Fassthal)
$$= \mathring{N}a_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O\ \dagger$$

(3) $3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2$ (Orthoclase from Striegau)
$$= \mathring{K}_6 \cdot \left(\hat{Al} \left\langle \begin{matrix} \hat{Si} \\ \hat{Si} \\ \hat{Si} \end{matrix} \right. \right)\ \ddagger$$

in the state of a molten glass with aqueous solutions of sodium silicate, $Na_2O \cdot 2_2SiO_2$ aq. of suitable concentration, at various temperatures (100°, 200–210°) for various periods (78 hours to five months) the following substance

$$(3\ Na_2O \cdot 3\ Al_2O_3 \cdot 15\ SiO_2 \cdot 7\tfrac{1}{2}\ H_2O)_2$$
$$= \left\{ \mathring{N}a_6 \left(\hat{Al} \left\langle \begin{matrix} \bar{Si} \\ \bar{Si} \\ \bar{Si} \end{matrix} \right. \right) \right\}_2 \cdot 15\ H_2O$$

was produced from Compounds 1 and 2, and the compound

$$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 12\ SiO_2 \cdot 6\ H_2O = \mathring{N}a_6(\hat{Si} \cdot \hat{Al} \cdot \hat{Si}) \cdot 6\ H_2O$$

from the silicate 3.

* Lemberg, *l.* c. 1883, p. 608, Expts. 35 and 36.
† Lemberg, *l.* c. 1885, pp. 992–3, Expts. 42 and 43.
‡ Lemberg, *l.* c. 1885, pp. 993–4, Expt. 47.

	Theory.	35	36	42	43
3 Na_2O	12.18	12.80	12.64	12.90	12.27
3 Al_2O_3	20.04	20.95	20.64	20.54	19.35
15 SiO_2	58.94	57.10	57.67	57.78	59.35
$7\frac{1}{2}$ H_2O	8.84	8.68	8.79	8.78	9.03
	—	0.47	0.30	—	—
	100.00	100.00	100.04	100.00	100.00

	Theory.	47
3 Na_2O	14.09	14.01
3 Al_2O_3	23.20	22.80
12 SiO_2	54.54	54.36
6 H_2O	8.17	8.53
	100.00	99.70

(c) The silicate

$$3\,Na_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2 \cdot 7\tfrac{1}{2}\,H_2O\ *$$

formed from the analcime from Fassthal, after a three weeks' treatment with potassium chloride solution at 100° and a further treatment for 100 hours at 200°, gave the compound

$$(3\,K_2O \cdot 3\,Al_2O_3 \cdot 15\,SiO_2 \cdot 1\tfrac{1}{2}\,H_2O)_2$$

$$= \left\{ \mathring{K}_6 \left(Al \begin{matrix} \diagup \overline{Si} \\ - \overline{Si} \\ \diagdown \overline{Si} \end{matrix} \right) \right\}_2 \cdot 3H_2O\dagger$$

	Theory.	42a	43a
3 K_2O	18.62	19.05	18.64
3 Al_2O_3	20.19	20.79	20.25
15 SiO_2	59.40	58.92	59.90
$1\frac{1}{2}$ H_2O	1.79	1.24	1.21
	100.00	100.00	100.00

(d) The behaviours towards acids of the following silicates:

(1) 0,5 Na_2O · 2,5 CaO · 3 Al_2O_3 · 18 SiO_2 · 17 H_2O (Stilbite from Berufjord)

$$= \mathring{N}a\mathring{C}a_{2,5}\ \hat{A}l \begin{matrix} \diagup \hat{S}i \\ - \hat{S}i \\ \diagdown \hat{S}i \end{matrix} \cdot 17\,H_2O\ddagger$$

(2) 0,5 Na_2O · 2,5 CaO · 3 Al_2O_3 · 18 SiO_2 · H_2O (Desmine from Farsern)

$$= \mathring{N}a\mathring{C}a_{2,5}\ \hat{A}l \begin{matrix} \diagup \hat{S}i \\ - \hat{S}i \\ \diagdown \hat{S}i \end{matrix} \cdot 20\,H_2O\ \S$$

(3) 0,5 K_2O · 2 Na_2O · 2,5 CaO · 5 Al_2O_3 · 18 SiO_2 · 28H_2O (Seebachite from Richmond) = $KNa_5Ca_{2,5}(\hat{S}i \cdot \overline{Al} \cdot \hat{S}i \cdot \overline{Al} \cdot \hat{S}i) \cdot 28\,H_2O$ ||

* Lemberg, *l.* c. 1885, p. 992, Expts. 42 and 43.
† Lemberg, *l.* c. 1885, pp. 992–3, Expts. 42a and 43a.
‡ Lemberg, *l.* c. 1885, pp. 987–8.
§ Lemberg, *l.* c. 1885, pp. 989, 990, 993.
|| Lemberg, *l.* c. 1885, pp. 972, 977–8.

(4) $0.5\ K_2O \cdot 2.5\ Na_2O \cdot 2\ CaO \cdot 5\ Al_2O_3 \cdot 18\ SiO_2 \cdot 28\ H_2O$ (Herschelite from Acireale)= $\mathring{K}\mathring{N}a_5\mathring{C}a_2(\hat{Si} \cdot \bar{Al} \cdot \hat{Si} \cdot \bar{Al} \cdot \hat{Si})\ 28\ H_2O$,* and their derivatives are shown in the following Tables I, II, III and IV, in which

V = Lemberg's Experiment Number.
S = The silicates used.
A = The salt solutions employed.
Z = The duration of the experiments.
T = The Temperature.
P = The Products obtained.

Table I

V.	S.	A.	Z.	T.	P.
39 a	$0.5\ Na_2O \cdot 2.5\ CaO \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 17\ H_2O$	KCl solution	1.5 Mths.	100°	$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 13\ H_2O$
39 b	$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 13\ H_2O$	NaCl ..	14 Days	100°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 16\ H_2O$
39 c	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 16\ H_2O$	NaCl ..	1355 Hrs.	210–220°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$
39 d	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 16\ H_2O$	$(Na_2O \cdot SiO_2 + NaCl)$ ..	75 Hrs.	195–205°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$
39 g	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 16\ H_2O$	(Borax+NaCl) ..	78 Hrs.	200–210°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$
39 h	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 16\ H_2O$	(Borax+NaCl) ..	78 Hrs.	200–210°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$
39 k	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 16\ H_2O$	$(Na_2HPO_4 + NaCl)$ ..	74 Hrs.	220°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$
39 e	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$	KCl ..	75 Hrs.	200°	$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot H_2O$
39 i	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$	KCl ..	78 Hrs.	210–215°	$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot H_2O$
39 l	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$	KCl ..	79 Hrs.	210°	$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot H_2O$
39 f	$3\ K_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot H_2O$	NaCl ..	6 Days	100°	$3\ Na_2O \cdot 3\ Al_2O_3 \cdot 18\ SiO_2 \cdot 8\ H_2O$

Analyses

	Theory.	39
0.5 Na_2O	1.66	1.40
2.5 CaO	7.53	7.43
3 Al_2O_3	16.26	16.48
18 SiO_2	58.09	57.97
17 H_2O	16.46	16.20
K_2O	—	0.52
	100.00	100.00

	Theory.	39a
3 K_2O	14.82	14.30
3 Al_2O_3	16.09	16.34
18 SiO_2	56.78	57.21
13 H_2O	12.31	12.85
	100.00	100.70

	Theory.	39b
3 Na_2O	10.00	8.89
3 Al_2O_3	16.45	16.72
18 SiO_2	58.07	58.14
16 H_2O	15.48	15.47
CaO	—	0.78
	100.00	100.00

* Lemberg, *l.* c. 1885, pp. 976, 979.

Theory.		39c	39d	39g	39h	39k	39f
3 Na_2O	10.84	10.61	10.94	11.27	11.07	10.74	10.81
3 Al_2O_3	17.84	17.56	17.99	17.74	17.56	18.21	17.71
18 SiO_2	62.94	62.56	62.54	62.22	62.68	62.32	62.87
8 H_2O	8.38	9.27	8.53	8.77	8.69	8.73	8.61
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Theory.		39e	39i	39l
3 Na_2O	16.73	16.66	16.87	16.63
3 Al_2O_3	18.10	18.15	18.00	18.72
18 SiO_2	64.09	64.27	63.89	63.41
H_2O	1.08	0.92	1.24	1.24
	100.00	100.00	100.00	100.00

The experiments shown in Table I indicate a replacement of the mono- and di-valent elements and a variation of the water in compounds of the type

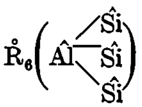


Table II

V.	S.	A.	Z.	T.	P.
40 a	0.5 Na_2O·2.5 CaO·3 Al_2O_3·18 SiO_2·20 H_2O	KCl sol.	1 Month	100°	3 K_2O·3 Al_2O_3·18 SiO_2·13 H_2O
40 b	3 K_2O·3 Al_2O_3·18 SiO_2·13 H_2O	NaCl ..	14 Days	100°	3 Na_2O·3 Al_2O_3·18 SiO_2·16 H_2O
40 c	3 Na_2O·3 Al_2O_3·18 SiO_2·16 H_2O	NaCl ..	1029 Hrs.	210–220°	3 Na_2O·3 Al_2O_3·18 SiO_2·8 H_2O
40 d	3 Na_2O·3 Al_2O_3·18 SiO_2·16 H_2O	(Na_2O·2 SiO_2+NaCl) ..	74 Hrs.	220°	3 Na_2O·3 Al_2O_3·18 SiO_2·8 H_2O
40 f	3 Na_2O·3 Al_2O_3·18 SiO_2·16 H_2O	(Borax+NaCl) ..	186 Hrs.	210–220°	3 Na_2O·3 Al_2O_3·18 SiO_2·8 H_2O
40 e	3 Na_2O·3 Al_2O_3·18 SiO_2·8 H_2O	KCl ..	79 Hrs.	210°	3 K_2O·3 Al_2O_3·18 SiO_2·H_2O
40 g	3 Na_2O·3 Al_2O_3·18 SiO_2·8 H_2O	KCl ..	79 Hrs.	210–220°	3 K_2O·3 Al_2O_3·18 SiO_2·H_2O
44	0.5 Na_2O·2.5 CaO·3 Al_2O_3·18 SiO_2·20 H_2O	20% Na_2CO_3 ..	15 Mnths.	100°	3 Na_2O·3 Al_2O_3·15 SiO_2·7½ H_2O
44 a	3 Na_2O·3 Al_2O_3·15 SiO_2·7½ H_2O	KCl ..	100 Hrs.	200°	3 K_2O·3 Al_2O_3·15 SiO_2·1½ H_2O
45	0.5 Na_2O·2.5 CaO·3 Al_2O_3·18 SiO_2·20 H_2O	25% Na_2O·SiO_2 ..	2 Mnths.	100°	3 Na_2O·3 Al_2O_3·12 SiO_2·6 H_2O
45 a	3 Na_2O·3 Al_2O_3·12 SiO_2·6 H_2O	KCl ..	3 Weeks	100°	3 K_2O·3 Al_2O_3·12 SiO_2·H_2O

Analyses

Theory.		40
0.5 Na_2O	1.60	0.91
2.5 CaO	7.31	7.60
3 Al_2O_3	15.96	16.18
18 SiO_2	56.36	56.62
20 H_2O	18.77	18.63
K_2O	—	0.24
	100.00	100.18

	Theory.	40a
3 K_2O	14.82	14.42
3 Al_2O_3	16.09	15.83
18 SiO_2	56.78	56.81
13 H_2O	12.31	12.94
	100.00	100.00

	Theory.	40b
3 Na_2O	10.00	9.74
3 Al_2O_3	16.45	16.35
18 SiO_2	58.07	57.09
16 H_2O	15.48	16.82
	100.00	100.00

	Theory.	40c	40d	40f
3 Na_2O	10.84	10.63	11.12	11.46
3 Al_2O_3	17.84	17.62	17.83	17.73
18 SiO_2	62.94	62.48	62.08	61.87
8 H_2O	8.38	9.27	8.97	8.94
	100.00	100.00	100.00	100.00

	Theory.	40e	40g
3 K_2O	16.73	17.18	17.11
3 Al_2O_3	18.10	18.51	18.39
16 SiO_2	64.09	62.77	62.95
H_2O	1.08	1.54	1.55
	100.00	100.00	100.00

	Theory.	44
3 Na_2O	12.18	11.84
3 Al_2O_3	20.04	19.79
15 SiO_2	58.94	59.93
7½ H_2O	8.84	8.44
	100.00	100.00

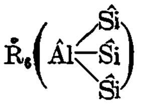
	Theory.	44a
3 K_2O	18.62	18.19
3 Al_2O_3	20.19	20.21
15 SiO_2	59.40	60.90
1⅓ H_2O	1.79	0.70
	100.00	100.00

	Theory.	45
3 Na_2O	14.09	13.72
3 Al_2O_3	23.20	22.14
12 SiO_2	54.54	55.26
6 H_2O	8.17	8.88
	100.00	100.00

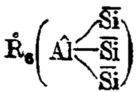
	Theory.	45a
3 K_2O	21.26	20.78
3 Al_2O_3	23.09	22.54
12 SiO_2	54.30	55.53
H_2O	1.35	1.15
	100.00	100.00

From the results shown in Table II it will be seen that there occur:

1. A substitution of the mono- and di-valent elements of compounds of the type



and a substitution of mono-valent elements in compounds of the types

 and $\dot{R}_6$ ($\hat{Si} \cdot \hat{Al} \cdot \hat{Si}$)

2. A conversion of the compounds of the type

$$\overset{\circ}{R}_6\left(\hat{Al}\begin{cases}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{cases}\right)$$

into those of the types

$$\overset{\circ}{R}_6\left(\hat{Al}\begin{cases}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{cases}\right) \text{ and } \overset{\circ}{R}_6(\hat{Si}\cdot\hat{Al}\cdot\hat{Si})$$

3. A change in the water-content is observable in some cases.

Table III.

V.	S.	A.	Z.	T.	P.
26 a	$0.5\,K_2O\cdot2\,Na_2O\cdot2.5\,CaO\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot28\,H_2O$	KCl Solution	2 Mths.	100°	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot24\,H_2O$
26 b	$0.5\,K_2O\cdot2\,Na_2O\cdot2.5\,CaO\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot28\,H_2O$	(8% K_2CO_3+15% KCl) „	70 Hrs.	200–210°	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot24\,H_2O$
26 c	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot24\,H_2O$	NaCl „	20 Days	100°	$5\,Na_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot27\,H_2O$
26 d	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot24\,H_2O$	(15% NaCl+5% Na_2CO_3) „	150 Hrs.	200–210°	$5\,Na_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot10\,H_2O$
26 f	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot24\,H_2O$	(15% NaCl+5% Na_2CO_3) „	150 Hrs.	200–210°	$5\,Na_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot10\,H_2O$
26 e	$5\,Na_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot10\,H_2O$	KCl „	100 Hrs.	200–215°	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot H_2O$
26 g	$5\,Na_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot10\,H_2O$	KCl „	100 Hrs.	210°	$5\,K_2O\cdot5\,Al_2O_3\cdot18\,SiO_2\cdot H_2O$

Analyses

Theory.		26
0.5 K_2O	1.94	2.00
2 Na_2O	5.09	4.92
2.5 CaO	5.78	5.89
5 Al_2O_3	21.04	21.66
18 SiO_2	44.54	44.30
28 H_2O	21.61	21.23
	100.00	100.00

Theory.		26a	26b
5 K_2O	18.87	18.85	18.65
5 Al_2O_3	20.48	20.43	20.49
18 SiO_2	43.35	43.75	44.21
24 H_2O	17.30	16.96	16.65
	100.00	99.99	100.00

Theory.		26c
5 Na_2O	12.98	12.89
5 Al_2O_3	21.44	21.27
18 SiO_2	45.23	45.44
27 H_2O	20.35	20.40
	100.00	100.00

Theory.		26d	26f
5 Na_2O	14.91	14.98	14.98
5 Al_2O_3	24.52	24.68	24.33
18 SiO_2	51.92	51.59	52.05
10 H_2O	8.65	8.75	8.64
	100.00	100.00	100.00

Theory.		26e	26g
5 K_2O	22.62	21.86	21.64
5 Al_2O_3	24.54	25.87	25.31
18 SiO_2	51.97	51.70	52.49
H_2O	0.87	0.57	0.56
	100.00	100.00	100.00

Table IV

V.	S.	A.	Z.	T.	P.
27 a	$0.5\,K_2O \cdot 2.5\,Na_2O \cdot 2\,CaO \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 28\,H_2O$	KCl Solution	1 Mth.	100°	$5\,K_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 24\,H_2O$
27 b	$0.5\,K_2O \cdot 2.5\,Na_2O \cdot 2\,CaO \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 28\,H_2O$	(15% KCl + 8% K_2CO_3) ..	150 Hrs.	210–220°	$5\,K_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 16\,H_2O$
27 c	$5\,K_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 24\,H_2O$	NaCl ..	18 Days	100°	$5\,Na_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 27\,H_2O$
27 d	$5\,Na_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 27\,H_2O$	(15% NaCl + 5% Na_2CO_3) ..	170 Hrs.	210–220°	$5\,Na_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 10\,H_2O$
27 e	$5\,Na_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 10\,H_2O$	KCl ..	75 Hrs.	200–210°	$5\,K_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot H_2O$
27 f	$5\,K_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot H_2O$	NaCl ..	10 Days	100°	$5\,Na_2O \cdot 5\,Al_2O_3 \cdot 18\,SiO_2 \cdot 10\,H_2O$

Analyses

	Theory.	27
$0.5\,K_2O$	1.94	1.27
$2.5\,Na_2O$	6.40	6.76
$2\,CaO$	4.55	5.05
$5\,Al_2O_3$	21.03	21.27
$18\,SiO_2$	44.49	44.12
$28\,H_2O$	21.59	21.57
	100.00	100.04

	Theory.	27a
$5\,K_2O$	18.87	18.67
$5\,Al_2O_3$	20.48	20.41
$18\,SiO_2$	43.35	44.08
$24\,H_2O$	17.30	16.84
	100.00	100.00

	Theory.	27b
$5\,K_2O$	20.02	19.55
$5\,Al_2O_3$	21.72	21.96
$18\,SiO_2$	45.99	46.34
$16\,H_2O$	12.27	12.15
	100.00	100.00

	Theory.	27c
$5\,Na_2O$	12.88	12.50
$5\,Al_2O_3$	21.44	21.28
$18\,SiO_2$	45.33	45.68
$27\,H_2O$	20.35	20.54
	100.00	100.00

	Theory.	27d	27f
$5\,Na_2O$	14.91	14.97	14.86
$5\,Al_2O_3$	24.52	24.52	24.44
$18\,SiO_2$	51.92	51.96	52.16
$10\,H_2O$	8.65	8.55	8.54
	100.00	100.00	100.00

	Theory.	27e
$5\,K_2O$	22.62	21.57
$5\,Al_2O_3$	24.54	25.20
$18\,SiO_2$	51.97	52.74
H_2O	0.87	0.49
	100.00	100.00

From the results given in Tables III and IV there is clearly a substitution of the mono- and di-valent elements in the type

$$\mathring{R}_{10}\,(\hat{Si} \cdot \overline{Al} \cdot \hat{Si} \cdot \overline{Al} \cdot \hat{Si})$$

and in one case (Table IV, No. 27d) a change in the water-content.

(e) The formation of compounds of the type *

$$5.5\,R_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 = \mathring{R}_{11}(\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{Si}).$$

On treating two molecules of $K_2O \cdot SiO_2$ with one molecule of $H_2O \cdot K_2O \cdot Al_2O_3$ Lemberg obtained the substance

$$0.5\,Na_2O \cdot 5\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 = \mathring{Na}\mathring{K}_{10}\,(\overline{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \overline{Si})\ †$$

* Lemberg, *l.* c. 1876, pp. 574–5.
† Expt. 1, *l.* c. p. 574.

On treating this silicate for a further period of 7 or 18 days at the ordinary temperature with variable quantities of solutions of sodium chloride, potassium chloride, etc.,* LEMBERG obtained compounds whose analyses corresponded to the general formula

$$5.5\,R_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2 = \mathring{R}_{11}(\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \bar{Si})$$

$Na_2O \cdot 4.5\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 2b)
$2\,Na_2O \cdot 3.5\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expts. 1a, 1g, 2a, 2c)
$2.5\,Na_2O \cdot 3\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expts. 1b, 1f, 2d)
$3\,Na_2O \cdot 2.5\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expts. 1c, 1e)
$3.5\,Na_2O \cdot 2\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 1d)
$5\,Na_2O \cdot 0.5\,K_2O \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 2)
$1.5\,K_2O \cdot 4\,MgO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 4b)
$2\,K_2O \cdot 3.5\,MgO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expts. 4a, 4c)
$2.5\,K_2O \cdot 3\,MgO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 4d)
$3\,K_2O \cdot 2.5\,MgO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 4)
$1.5\,K_2O \cdot 4\,CaO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expts. 3a, 3b, 3c)
$2\,K_2O \cdot 3.5\,CaO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 3d)
$2.25\,K_2O \cdot 3.25\,CaO \cdot 6\,Al_2O_3 \cdot 16\,SiO_2$ (Expt. 3).

Theory.		1
$0.5\,Na_2O$	1.50	1.83
$5\,K_2O$	22.67	22.75
$6\,Al_2O_3$	29.52	29.38
$16\,SiO_2$	46.31	46.04
	100.00	100.00

Theory.		2b
Na_2O	3.02	2.55
$4.5\,K_2O$	20.56	21.21
$6\,Al_2O_3$	29.75	30.60
$16\,SiO_2$	46.67	45.64
	100.00	100.00

Theory.		1a	1g	2a	2c
$2\,Na_2O$	6.12	6.41	6.67	5.98	5.91
$3.5\,K_2O$	16.25	16.00	15.40	16.37	16.79
$6\,Al_2O_3$	30.22	29.99	29.88	30.40	30.30
$16\,SiO_2$	47.41	47.60	48.05	47.25	47.00
	100.00	100.00	100.00	100.00	100.00

Theory.		1b	1f	2d
$2.5\,Na_2O$	7.72	7.54	7.52	7.54
$3\,K_2O$	14.04	14.12	14.03	14.71
$6\,Al_2O_3$	30.46	29.74	30.00	30.00
$16\,SiO_2$	47.78	48.60	48.45	47.75
	100.00	100.00	100.00	100.00

* In the cases mentioned the salt solutions were of a definite concentration. The salts were: NaCl-, KCl-, $MgCl_2$-, $CaCl_2$-, (NaCl+KCl)-, ($MgCl_2$+KCl)-, ($CaCl_2$+KCl).

Theory.		1c	1e
3 Na_2O	9.33	8.97	8.78
2.5 K_2O	11.79	11.89	12.10
6 Al_2O_3	30.71	30.12	30.13
16 SiO_2	48.17	49.02	48.99
	100.00	100.00	100.00

Theory.		1d
3.5 Na_2O	10.97	11.19
2 K_2O	9.57	8.95
6 Al_2O_3	30.96	30.29
16 SiO_2	48.50	49.57
	100.00	100.00

Theory.		2
5 Na_2O	16.07	15.60
0.5 K_2O	2.43	3.21
6 Al_2O_3	31.73	31.20
16 SiO_2	49.77	49.99
	100.00	100.00

Theory.		4b
1.5 K_2O	7.52	7.94
4 MgO	8.54	8.33
6 Al_2O_3	32.68	32.29
16 SiO_2	51.26	51.44
	100.00	100.00

Theory.		4a	4c
2 K_2O	9.89	10.03	10.01
3.5 MgO	7.36	6.97	7.03
6 Al_2O_3	32.22	31.72	31.60
16 SiO_2	50.53	51.28	51.36
	100.00	100.00	100.00

Theory.		4d
2.5 K_2O	12.19	11.59
3 MgO	6.23	6.37
6 Al_2O_3	31.76	31.69
16 SiO_2	49.82	50.35
	100.00	100.00

Theory.		4
3 K_2O	14.43	13.72
2.5 MgO	5.12	4.94
6 Al_2O_3	31.32	31.80
16 SiO_2	49.13	49.19
	100.00	99.65

Theory.		3a	3b	3c
1.5 K_2O	7.28	7.75	6.42	7.32
4 CaO	11.57	11.07	12.14	10.99
6 Al_2O_3	31.60	30.91	31.20	31.00
16 SiO_2	49.55	50.27	50.24	50.79
	100.00	100.00	100.00	100.10

Theory.		3d
2 K_2O	9.61	8.81
3.5 CaO	10.02	10.10
6 Al_2O_3	31.29	31.03
16 SiO_2	49.08	50.06
	100.00	100.00

Theory.		3
2.25 K_2O	10.76	10.87
3.25 CaO	9.26	9.22
6 Al_2O_3	31.13	30.64
16 SiO_2	48.85	49.23
	100.00	99.96

The Topaz Group

The following analyses of the Topazes conform to compounds of the type

$$\hat{Al} \cdot \hat{Si} \cdot \hat{Al} = 6\ Al_2O_3 \cdot 6\ SiO_2$$

and to the following formulæ :

(a) $Si_6Al_{12}O_{26}\ Fl_8$,
(b) $Si_6Al_{12}O_{25 \cdot 5}Fl_9$,
(c) $Si_6Al_{12}O_{25}\ Fl_{10}$,
(d) $Si_6Al_{12}O_{24 \cdot 5}Fl_{11}$,
(e) $Si_6Al_{12}O_{24}\ Fl_{12}$.

	SiO_2	Al_2O_3	Fl	Total	Source	Analyst
				(a) $Si_6Al_{12}O_{26}Fl_8$.		
Theory	33.97	57.74	14.34	106.05	—	—
I	34.24	57.45	14.99	107.37	Schneckenstein	Berzelius[1] *
XII	34.36	57.74	15.02	107.12	Finbo	Berzelius[2]
XXII	34.01	58.38	15.06	107.45	Brazil	Berzelius[3]
				(b) $Si_6Al_{12}O_{25 \cdot 5}Fl_9$.		
Theory	33.62	57.14	15.97	106.73	—	—
XXIV	33.73	57.39	16.12	107.24	Brazil	Rammelsberg[4]
XXV	33.15	57.01	16.04	106.20	Pikes Peak	Hillebrand[5]
				(c) $Si_6Al_{12}O_{25}Fl_{10}$.		
Theory	33.25	56.55	17.56	107.36	—	—
IV	33.35	56.53	17.69	107.57	Altenberg	Klemm[6]
V	33.23	56.20	17.37	106.80	Altenberg	Klemm[7]
VI	33.38	56.32	17.26	106.96	Altenberg	Klemm[8]
XIV	33.72	56.10	17.20	107.02	Finbo	Klemm[9]
XV	33.57	56.30	17.00	106.87	Finbo	Klemm[10]
XVI	33.64	56.24	17.12	107.00	Finbo	Klemm[11]
XVIII	33.68	56.36	17.11	107.15	Miask	Klemm[12]
XIX	33.19	56.72	17.09	107.00	Miask	Klemm[13]
XXI	33.24	57.02	17.64	108.73	Tasmania	Sommerland[14]
				(d) $Si_6Al_{12}O_{24 \cdot 5}Fl_{11}$.		
Theory	32.93	55.97	19.12	108.02	—	—
III	33.53	56.54	18.62	108.69	Schneckenstein	Rammelsberg[15]
X	32.28	55.86	18.28	106.42	Zinnwald	Rammelsberg[16]
XI	33.27	56.76	18.54	108.67	Schlaggenwald	Rammelsberg[17]
XX	33.56	56.28	18.30	106.14	Adun-Tschilon	Rammelsberg[18]

* References to the Literature are given on p. 438 *et seq.*

The Epidotes

The following analyses of the Epidotes conform to compounds of the type

$$\hat{Si} \cdot \hat{Al} \cdot \hat{Al} \cdot \hat{Si} = 6\,Al_2O_3 \cdot 12\,SiO_2$$

or to the general formula :

$$4\,H_2O \cdot 16\,CaO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \quad (12\,R_2O_3 = mFe_2O_3\,nAl_2O_3).$$

(a) $4\,H_2O \cdot 16\,CaO \cdot 2\,Fe_2O_3 \cdot 10\,Al_2O_3 \cdot 24\,SiO_2$.
(b) $4\,H_2O \cdot 16\,CaO \cdot 2.25\,Fe_2O_3 \cdot 9.75\,Al_2O_3 \cdot 24\,SiO_2$.
(c) $4\,H_2O \cdot 16\,CaO \cdot 2.5\,Fe_2O_3 \cdot 9.5\,Al_2O_3 \cdot 24\,SiO_2$.
(d) $4\,H_2O \cdot 16\,CaO \cdot 2.75\,Fe_2O_3 \cdot 9.25\,Al_2O_3 \cdot 24\,SiO_2$.
(e) $4\,H_2O \cdot 16\,CaO \cdot 3\,Fe_2O_3 \cdot 9\,Al_2O_3 \cdot 24\,SiO_2$.
(f) $4\,H_2O \cdot 16\,CaO \cdot 3.25\,Fe_2O_3 \cdot 8.75\,Al_2O_3 \cdot 24\,SiO_2$.
(g) $4\,H_2O \cdot 16\,CaO \cdot 3.5\,Fe_2O_3 \cdot 8.5\,Al_2O_3 \cdot 24\,SiO_2$.
(h) $4\,H_2O \cdot 16\,CaO \cdot 3.75\,Fe_2O_3 \cdot 8.25\,Al_2O_3 \cdot 24\,SiO_2$.
(i) $4\,H_2O \cdot 16\,CaO \cdot 4\,Fe_2O_3 \cdot 8\,Al_2O_3 \cdot 24\,SiO_2$.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	H_2O	FeO	Total	Source	Analyst
	(a) $4\,H_2O \cdot 16\,CaO \cdot 2\,Fe_2O_3 \cdot 10\,Al_2O_3 \cdot 24\,SiO_2$.								
Theory	38.44	27.21	8.54	23.90	1.91		100.00		
III	39.18	26.52	8.21	23.80	2.20		100.00	Zöptau	Nauke[1]*
XVI	38.42	26.62	8.72	23.66	2.46		99.88	Sustenhorn	Stockar-Escher[2]
XVII	38.43	26.18	8.77	24.13	2.46		99.97	Sustenhorn	Stockar-Escher[3]
XX	37.66	27.36	8.90	23.90	2.33		100.15	Caverdiras	Stockar-Escher[4]
XXI	38.08	27.74	8.27	23.53	2.04		99.66	Maggiatal	Stockar-Escher[5]
XXII	38.28	27.53	8.66	22.87	2.41		99.75	Formazzatal?	Stockar-Escher[6]
XLIV	37.92	27.90	9.10	22.81	2.02		99.75	Pargas	Wilk[7]
	(b) $4\,H_2O \cdot 16\,CaO \cdot 2.25\,Fe_2O_3 \cdot 9.75\,Al_2O_3 \cdot 24\,SiO_2$.								
Theory	38.28	26.43	9.57	23.81	1.91		100.00		—
XIV	37.96	26.35	9.71	23.77	2.02		99.81	Guttannen	Stockar-Escher[8]
XV	38.13	26.42	9.74	23.30	2.02		99.61	Guttannen	Stockar-Escher[9]
XXXIV	37.87	24.72	9.96	23.10	2.82	0.36	100.14a	Mainland	Heddle[10]
	(c) $4\,H_2O \cdot 16\,CaO \cdot 2.5\,Fe_2O_3 \cdot 9.5\,Al_2O_3 \cdot 24\,SiO_2$.								
Theory	38.13	25.65	10.59	23.72	1.91		100.00		—
XIII	38.99	25.75	9.99	23.76	2.05	0.61 MgO	100.16	Guttannen	Schneider[11]
XLI	38.84	25.45	10.88	22.62	2.41		100.20	Arendal	Richter[12]
	(d) $4\,H_2O \cdot 16\,CaO \cdot 2.75\,Fe_2O_3 \cdot 9.25\,Al_2O_3 \cdot 24\,SiO_2$.								
Theory	38.00	24.90	11.60	23.62	1.88	—	100.00	—	—
LIII	37.47	24.08	10.60	22.19	2.24	2.81	99.40	Achtenskoi	Hermann[13]
LIX	38.20	24.02	12.20	21.59	2.16	0.57 MnO	99.84b	Rowe, Mass.	A. G. Dana[14]
	(e) $4\,H_2O \cdot 16\,CaO \cdot 3\,Fe_2O_3 \cdot 9\,Al_2O_3 \cdot 24\,SiO_2$.								
Theory	37.84	24.12	12.61	23.54	1.89	—	100.00	—	—
VIII	38.60	23.08	12.34	24.17	1.88	0.95	101.02	Sulzbachtal	Mauthner[15]
IX	36.90	24.36	12.40	23.54	2.01	0.72	100.00c	Sulzbachtal	Laspeyres[16]
XXXII	38.26	24.75	11.07	23.63	2.26	0.56	100.53	Quenast	Renard[17]
XXXVII	37.32	22.85	11.56	22.13	2.93	1.86	99.32d	Arendal	Hermann[18]

a Incl. 0.54 MnO · 0.77 MgO.
b Incl. 0.07 MnO.
c. Incl. 0.12 MgO · 0.37 Alkalies.
d Incl. 0.77 MgO.

* *For references see p. 438.*

	SiO_2	Al_2O_3	Fe_2O_3	CaO	H_2O	FeO	Total	Source	Analyst
(f) $4\ H_2O \cdot 16\ CaO \cdot 3.25\ Fe_2O_3 \cdot 8.75\ Al_2O_3 \cdot 24\ SiO_2$.									
Theory	37.70	23.37	13.60	23.45	1.88		100.00	—	—
IV	38.37	22.09	13.77	22.90	2.11		99.24	Sulzbachtal	v. Drasche[19]
VI	37.83	23.43	13.31	23.47	2.06	0.48	100.58	Sulzbachtal	Ludwig[20]
(g) $4\ H_2O \cdot 16\ CaO \cdot 3.5\ Fe_2O_3 \cdot 8.5\ Al_2O_3 \cdot 24\ SiO_2$.									
Theory	37.55	22.61	14.60	23.36	1.88		100.00	—	—
V	37.83	22.63	14.02	23.27	2.05	0.93	100.73	Sulzbachtal	Ludwig[21]
XXX	36.71	22.61	14.47	23.67	1.92	0.62	100.00	"Bourg d'Osians"	Laspeyres[22]
LVIII	37.04	22.99	14.19	24.09	2.16		100.47	Hereroland	Wulf[23]
(h) $4\ H_2O \cdot 16\ CaO \cdot 3.75\ Fe_2O_3 \cdot 8.25\ Al_2O_3 \cdot 24\ SiO_2$.									
Theory	37.40	21.86	15,59	23.28	1.87		100.00	—	—
VII	37.11	21.90	16,00	23.19	2.03		100.23	Sulzbachtal	Rammelsberg[24]
(i) $4\ H_2O \cdot 16\ CaO \cdot 4\ Fe_2O_3 \cdot 8\ Al_2O_3 \cdot 24\ SiO_2$.									
Theory	37.27	21.11	16.56	23.19	1.87	—	100.00	—	—
XXIII	37.65	20.64	16.50	22.32	2.06	0.49MnO	100.12	Traversella	Scheerer[25]
XXVIII	37.56	20.78	16.49	22.70	2.09	0.29 MgO	99.91	"Bourg d'Osians"	Scheerer[26]
XXIX	37.35	22.02	15.67	22.54	2.35	—	99.93	"Bourg d'Osians"	Stockar-Escher[27]
XXXVII	38.76	20.36	16.35	23.71	2.00	0.44 MgO	101.67	Arendal	Rammelsberg[28]
XL	37.59	20.73	16.57	22.64	2.11	0.41 MgO	100.05	Arendal	Scheerer[29]

The Granite Group

A number of Granites examined by K. H. Schneer may be expressed by the general formula :

$$18\ RO \cdot 6\ R_2O_3 \cdot 18\ SiO_2 \text{ and } 16\ RO \cdot 6\ R_2O_3 \cdot 16\ SiO_2$$

as may be ascertained from the following Table :

	%							Molecules						
No.	CaO	FeO	MnO	Al_2O_3	Fe_2O_3	SiO_2	H_2O	CaO	FeO	MnO	Al_2O_3	Fe_2O_3	SiO_2	H_2O
Theory	33.25	1.22	—	6.92	21.72	36.89								
1	33.59	1.17	—	7.44	20.94	36.56	—	17.5	0.5	—	2	4	18	—
Theory	32.12	1.82	0.60	6.88	21.59	36.68	0.31							
2	32.36	1.91	0.48	7.35	21.58	36.33	0.48	17	0.75	0.25	2	4	18	0.5
Theory	32.12	2.43	—	6.88	21.59	36.68	0.30							
3	31.51	2.88	—	7.07	22.51	35.97	0.25	17	1	—	2	4	18	0.5
Theory	33.52	1.25	0.61	12.39	13.88	37.73	0.62							
4	33.55	1.68	0.28	11.99	14.79	37.53	0.48	17.25	0.5	0.25	3.5	2.5	18	1
Theory	34.22	1.25	—	13.36	12.57	37.96	0.64							
5	34.01	1.71	0.54	13.29	13.01	37.52	0.53	17.5	0.5	—	3.75	2.25	18	1
Theory	32.46	3.85		16.37	8.56	38.76	—							
6	31.98	4.46	0.57	16.29	8.73	37.96	0.22	16.25	1.75	—	4.5	1.5	18	—
Theory	32.06	2.74	—	13.72	14.60	36.89	—							
7	32.73	2.54	—	13.73	14.03	37.18	—	15	1	—	3.75	2.25	16	

The

The following analyses of the

(a) $\bar{Si} \cdot \hat{Al} \cdot \dot{\bar{Si}} \cdot \hat{Al} \cdot \dot{Si} = 6\,Al_2O_3 \cdot 15\,SiO_2$,

(b) $\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \dot{\bar{Si}} = 6\,Al_2O_3 \cdot 16\,SiO_2$,

(a) Mesolites of the type

$\bar{Si} \cdot \hat{Al} \cdot \bar{Si} \cdot \hat{Al} \cdot \dot{Si} = 6\,Al_2O_3 \cdot 15\,SiO_2$.

			Source	Analyst
1	$9\,MO \cdot 2\,(6\,Al_2O_3 \cdot 15\,SiO_2) \cdot 36\,H_2O$	$9\,MO = 3\,Na_2O \cdot 6\,CaO$	Antrimolite Bengune	Thomson
2	$11\,MO \cdot 2\,(6\,Al_2O_3 \cdot 15\,SiO_2) \cdot 26\,H_2O$	$11\,MO = 5\,Na_2O \cdot 6\,CaO$	Eisenach	Luedecke

(b) Mesolites of the type

$\bar{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \dot{Si} = 6\,Al_2O_3 \cdot 16\,SiO_2$

			Source	Analyst
3	$10\,MO \cdot 2\,(6\,Al_2O_3 \cdot 16\,SiO_2)\,30\,H_2O$	$10\,MO = 4\,Na_2O \cdot 6\,CaO$	Sandy Cove, N.S.	Marsh
4	$11\,MO \cdot 2\,(6\,Al_2O_3 \cdot 16\,SiO_2)\,40\,H_2O$	$11\,MO = 5\,Na_2O \cdot 6\,CaO$	Caranja Isle	Thomson
5	$12\,MO \cdot 2\,(6\,Al_2O_3 \cdot 16\,SiO_2)\,24\,H_2O$	$12\,MO = 4\,Na_2O \cdot 8\,CaO$	Harringtonite	Thomson

(c) Mesolites of the type

$\hat{Si} \cdot \hat{Al} \cdot \dot{Si} \cdot \hat{Al} \cdot \hat{Si} = 6\,Al_2O_3 \cdot 17\,SiO_2$

			Source	Analyst
6	$9\,MO \cdot 2\,(6\,Al_2O_3 \cdot 17\,SiO_2) \cdot 32\,H_2O$	$9\,MO = 2\,Na_2O \cdot 7\,CaO$	Iceland	Fuchs & Gehlen
7	$11\,MO \cdot 2\,(6\,Al_2O_3 \cdot 17\,SiO_2) \cdot 30\,H_2O$	$11\,MO = 4\,Na_2O \cdot 7\,CaO$	Iceland	Breidenstein

(d) Mesolites of the type

$\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si} = 6\,Al_2O_3 \cdot 18\,SiO_2$

			Source	Analyst
8	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 30H_2O$	$12MO = 4\,Na_2O \cdot 8\,CaO$	Niederkirchen	Riegel
9	" " " "	" " "	Tirol	Fuchs & Gehlen
10	" " " "	" " "	Antrimolite	Heddle
11	" " " "	" " "	Bengune	Heddle
12	" " " "	" " "	Skye	Heddle
13	" " " "	" " "	Skye	Heddle

Mesolites

Mesolites conform to the following types:

(c) $\hat{Si} \cdot \hat{Al} \cdot Si \cdot \hat{Al} \cdot \hat{Si} = 6\,Al_2O_3 \cdot 17\,SiO_2$,

(d) $\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si} = 6\,Al_2O_3 \cdot 18\,SiO_2$.

or the general formula

m $MO \cdot 2\,(6\,Al_2O_3 \cdot 15\,SiO_2) \cdot n\,H_2O$.

	SiO_2	Al_2O_3	CaO	Na_2O	H_2O	MgO	Total
Theory	42.92	29.18	8.01	4.43	15.46	—	100.00
VII	43.47	30.26	7.50	4.10*	15.32	0.19 FeO	100.94
Theory	43.50	29.57	8.12	7.49	11.31	—	100.00
II	43.83	29.04	7.84	7.80	11.75	—	100.26

or the general formula

m $MO \cdot 2\,(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot n\,H_2O$.

	SiO_2	Al_2O_3	CaO	Na_2O	H_2O	MgO	Total
Theory	44.98	28.68	7.87	5.81	12.66	—	100.00
XXXII	45.39	28.09	7.55	5.28	12.71	0.49 K_2O	99.51
Theory	42.58	27.14	7.45	6.87	15.96	—	100.00
XXXIX	42.70	27.50	7.61	7.00	14.71	—	99.52
Theory	44.95	28.65	11.21	5.80	10.11	—	100.00
XI	44.84	28.48	10.68	5.56	10.28	—	99.84

or the general formula

m $MO \cdot 2\,(6\,R_2O_3 \cdot 17\,SiO_2) \cdot n\,H_2O$.

	SiO_2	Al_2O_3	CaO	Na_2O	H_2O	MgO	Total
Theory	46.83	28.10	9.00	2.84	13.83	—	100.00
XXVI	46.58	27.57	9.10	3.64	13.17	0.08	100.14
Theory	45.90	27.54	8.82	5.58	12.15	—	100.00
XXIII	45.78	27.53	9.00	5.03	12.30	0.31 K_2O	100.13

or the general formula

m $MO \cdot 2\,(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O$.

	SiO_2	Al_2O_3	CaO	Na_2O	H_2O	MgO	Total
Theory	46.76	26.49	9.70	5.37	11.68	—	100.00
I	46.65	27.40	9.26	4.91	12.00	—	100.22
V	46.04	27.00	9.61	5.20	12.36	—	100.21
VIII	47.07	26.23	9.88	4.89	12.24	—	100.31
IX	45.98	26.18	10.78	4.54	13.00	—	100.48
XIII	46.70	26.62	9.08	5.39	12.83	—	100.63
XIV	46.72	26.70	8.90	5.40	12.92	—	100.64

* Determined by *Thomson* as K_2O.

			Source	Analyst
	$12MO \cdot 2(6Al_2O_3 \cdot 18\,SiO_2) \cdot 30H_2O$	$12MO = 4\,Na_2O \cdot 8\,CaO$		
14	,, ,, ,, ,,	,, ,, ,,	Skye	Heddle
15	,, ,, ,, ,,	,, ,, ,,	Naalsjö	Berzelius
16	,, ,, ,, ,,	,, ,, ,,	Naalsjö	Heddle
17	,, ,, ,, ,,	,, ,, ,,	Naalsjö	Fuchs and Gehlen
18	,, ,, ,, ,,	,, ,, ,,	Naalsjö	Durscher
19	,, ,, ,, ,,	,, ,, ,,	Stromö	E. E. Schmid
20	,, ,, ,, ,,	,, ,, ,,	Berufjord	S. v. Waltershausen
21	,, ,, ,, ,,	,, ,, ,,	Iceland	Fuchs and Gehlen
22	,, ,, ,, ,,	,, ,, ,,	Iceland	Fuchs and Gehlen
23	,, ,, ,, ,,	,, ,, ,,	Iceland	E. E. Schmid
24	,, ,, ,, ,,	,, ,, ,,	Iceland	Lemberg
25	,, ,, ,, ,,	,, ,, ,,	Port George, N.S.	How
26	,, ,, ,, ,,	,, ,, ,,	Port George, N.S.	How
27	,, ,, ,, ,,	,, ,, ,,	Cape Blomidon	Marsh
28	,, ,, ,, ,,	,, ,, ,,	Atacama, Chili	Darapsky
29	$14MO \cdot 2(6\,Al_2O_3 \cdot 18SiO_2) \cdot 44H_2O$	$14MO = 3Na_2O \cdot 11\,CaO$	Fritz Island, Pa.	Sadtler

The

The following analyses of the minerals of the

$$\begin{aligned}
&\text{A. } \bar{R} \cdot \hat{Si} \cdot \bar{R} &&= 5\,R_2O_3 \cdot 6\,SiO_2,\\
&\text{B. } \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} &&= 5\,R_2O_3 \cdot 12\,SiO_2,\\
&\text{C. } \hat{R} \cdot \hat{Si} \cdot \hat{R} &&= 6\,R_2O_3 \cdot 6\,SiO_2,\\
&\text{D. } \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} &&= 6\,R_2O_3 \cdot 12\,SiO_2,\\
&\text{E. } \bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} &&= 6\,R_2O_3 \cdot 16\,SiO_2,\\
&\text{F. } \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} &&= 6\,R_2O_3 \cdot 18\,SiO_2.
\end{aligned}$$

A. Compounds of the type

$\bar{R} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 6\,SiO_2$

			Source	Analyst
1	$12MO \cdot 2\,(5\,Al_2O_3 \cdot 6SiO_2) \cdot 12H_2O$	$12\,MO = 8\,FeO \cdot 4\,MgO$	St. Marcel	Kobell
2	$13MO \cdot 2\,(5\,Al_2O_3 \cdot 6\,SiO_2) \cdot 9\,H_2O$	$13MO = 10FeO \cdot 2.5\,MgO \cdot 0.5\,MnO$	Leeds, Canada	Hunt

B. Compounds of the type

$\bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 12\,SiO_2$

			Source	Analyst
3	$13MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2) \cdot 11H_2O$	$13MO = 9.25\,FeO \cdot 3.75\,MgO$	St. Marcel	Damour

	SiO_2	Al_2O_3	CaO	Na_2O	H_2O	MgO	Total
Theory	46.76	26.49	9.70	5.37	11.68	—	100.00
XV	46.26	26.48	10.00	4.98	13.04	—	100.76
XVII	46.80	26.50	9.87	5.40	12.30	—	100.87
XVIII	46.80	26.46	9.08	5.14	12.28	—	99.76
XIX	47.00	26.13	9.35	5.47	12.25	—	100.20
XX	47.50	26.10	9.15	4.57	12.80	—	100.12
XXI	47.40	27.05	9.16	4.69	12.69	0.06	101.05
XXII	46.41	26.24	9.68	4.46	13.76	0.01	100.97
XXIV	46.78	25.66	10.06	4.79	12.31	—	99.60
XXV	47.46	25.35	10.04	4.87	12.41	—	100.13
XXVII	47.13	26.52	10.36	4.50	12.59	—	101.12
XXVIII	45.96	26.69	9.48	5.09	12.78	—	100.00
XXIX	46.66	26.48	9.63	4.83	12.25	—	99.85
XXX	46.71	26.68	9.55	5.68	11.42	—	100.04
XXXI	45.89	27.55	9.13	5.09	12.79	0.48 K_2O	100.93
XXXVI	46.74	25.99	9.11	5.23	12.41	—	99.48
Theory	43.39	24.59	12.37	3.73	15.92	—	100.00
XXXIII	43.29	25.02	12.15	3.40	16.01	—	99.87

Clintonite Group*

Clintonite group conform to the following types:

G. $\hat{Si}\!\left\langle\begin{matrix}\bar{R}\\ \bar{R}\\ \bar{R}\end{matrix}\right. = 7.5\,R_2O_3 \cdot 6\,SiO_2,$

H. $\bar{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \bar{R} = 8\,R_2O_3 \cdot 12\,SiO_2,$

J. $\hat{Si}\!\left\langle\begin{matrix}\hat{R}\\ \hat{R}\\ \hat{R}\end{matrix}\right. = 9\,R_2O_3 \cdot 6\,SiO_2,$

K. $\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} = 9\,R_2O_3 \cdot 12\,SiO_2.$

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	26.74	37.89	—	21.40	—	5.94	—	8.03	100.00
IX	25.75	37.50	—	21.00	—	6.20	—	7.80	98.25
Theory	26.12	36.99	—	26.11	1.28	3.62	—	5.88	100.00
XXXI	26.30	37.10	—	25.92	0.93	3.66	—	6.10	100.01

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 12.SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	26.23	37.27	—	24.27	—	5.11	—	7.22	100.00
XI	25.50	38.13	—	23.58	—	5.19	—	6.90	99.30

* Known in Germany as the Sprödglimmer or "brittle micas."

C. Compound

$\hat{R} \cdot \hat{Si} \cdot \hat{R} = $ (

4	$10\,MO \cdot 2(6\,R_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$10\,MO = 7\,FeO \cdot 3\,MgO \cdot 12\,R_2O_3 = 8.75\,Al_2O_3 \cdot 3.25\,Fe_2O_3$
5	$11\,MO \cdot 2(6\,R_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$11\,MO = 5\,MgO \cdot 5.5\,FeO \cdot 0.5\,CaO \cdot 12\,R_2O_3 = 11.25\,Al_2O_3 \cdot 0.75\,Fe_2O_3$
6	$11\,MO \cdot 2(6\,R_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$11\,MO = 4.75\,MgO \cdot 0.25\,MnO \cdot 5.5\,FeO \cdot 0.5\,CaO \cdot 12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$
7	$11\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 12\,H_2O$	$11\,MO = 11\,FeO$
8	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2)$	$12\,MO = 12\,FeO$
9	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$12\,MO = 11.5\,FeO \cdot 0.5\,H_2O$
10	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$12\,MO = 10.5\,FeO \cdot 1.5\,MgO$
11	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 12\,H_2O$	$12\,MO = 7.75\,FeO \cdot 4.25\,MgO$
12	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 12\,H_2O$	$12\,MO = 9.75\,FeO \cdot 2.25\,MgO$
13	$13\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 12\,H_2O$	$13\,MO = 11.75\,FeO \cdot 0.75\,MgO \cdot 0.25\,MnO \cdot 0.25\,CaO$
14	$13\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 12\,H_2O$	$13\,MO = 11.75\,FeO \cdot 0.75\,MgO \cdot 0.25\,MnO \cdot 0.25\,CaO$
15	$13\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_3) \cdot 12\,H_2O$	$13\,MO = 7.5\,FeO \cdot 0.5\,MnO \cdot 5\,MgO$
16	$15\,MO \cdot 2(6\,Al_2O_3 \cdot 6\,SiO_2) \cdot 11\,H_2O$	$15\,MO = 12\,Fe\,O \cdot 3\,MgO$

D. Compound

$\hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} = $ 6

17	$10\,MO \cdot 2(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 8\,H_2O$	$10\,MO = 6\,FeO \cdot 3\,MnO \cdot 0.5\,MgO \cdot 0.5\,CaO \cdot 12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Li
18	$19\,MO \cdot 2(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 14\,H_2O$	$19\,MO = 15.5\,FeO \cdot 3.5\,MnO$	Na Is

E. Compound

$\hat{Si} \cdot \hat{Al} \cdot \hat{Si} \cdot \hat{Al} \cdot \hat{Si} = 6$ A

19	$13\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 12\,H_2O$	$13\,MO = 12.5\,FeO \cdot 0.5\,MgO$	Vi

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Hermann	Theory	24.52	30.39	17.71	17.17	—	4.08	—	6.13	100.00
	XXVI	24.54	30.72	17.28	17.30	—	3.75	—	6.38	99.97
Suida	Theory	25.70	41.11	4.29	14.19	—	7.16	1.00	6.46	100.00
	X	26.03	42.33	4.09	14.32	—	7.30	0.35	6.56	100.98
Heddle	Theory	25.91	42.21	2.87	14.05	0.64	6.84	1.00	6.48	100.00
	XXI	25.36	41.74	3.90	13.93	0.92	6.82	0.90	6.57	100.14
Delesse	Theory	24.39	41.47	—	26.83	—	—	—	7.31	100.00
	VIII	24.10	40.71	—	27.10	—	—	—	7.24	99.15
Erdmann	Theory	25.64	43.59	—	30.77	—	—	—	—	100.00
	XXIV	24.96	43.83	—	31.21	—	—	—	—	100.00
Smith	Theory	24.41	41.50	—	27.69	—	—	—	6.40	100.00
	XXVIII	24.10	39.80	—	27.55	0.30	(K_2O+Na_2O)	—	6.50	98.25
Renard	Theory	24.59	41.78	—	25.45	—	2.05	—	6.13	100.00
	XIII	24.90	40.36	—	26.17	—	2.54	—	6.23	100.23
Damour	Theory	24.93	42.38	—	19.33	—	5.88	—	7.48	100.00
	VI	24.40	42.80	—	19.17	—	6.17	—	6.90	99.44
A. Sipöcz	Theory	24.39	41.46	—	23.78	—	3.05	—	7.32	100.00
	IV	24.90	40.99	0.55	24.28	—	3.33	—	7.82	101.87
L. Smith	Theory	23.47	39.90	—	27.58	0.58	0.98	0.46	7.03	100.00
	XXIX	23.94	39.52	—	28.05	0.52	0.80	0.45	7.08	100.36
L. Smith	Theory	23.47	39.90	—	27.58	0.58	0.98	0.46	7.03	100.00
	XXX	23.20	40.21	—	27.25	—	0.95	0.83	6.97	99.41
Heddle	Theory	24.53	41.70	--	18.40	1.21	6.81	—	7.35	100.00
	XX	24.47	41.34	0.38	18.52	0.91	6.80	0.30	6.98	99.70
Kobell	Theory	23.03	39.15	—	27.64	—	3.84	—	6.34	100.00
	XXVII	23.01	40.26	—	27.40	—	3.97	—	6.34	100.98

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	40.52	31.58	4.50	11.99	5.99	0.57	0.79	4.06	100.00
XVIII	40.55	30.80	3.82	12.46	6.51	0.45	1.29	4.12	100.00
Theory	33.64	28.59	—	26.07	5.81	—	—	5.89	100.00
XXXII	33.20	29.00	—	25.93	6.00	0.24	—	5.60	99.97

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 16\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	44.87	28.60	—	21.03	—	0.46	—	5.04	100.00
XII	44.79	29.71	—	20.75	—	0.62	—	4.93	100.80

F. Compounds of the type

$$\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 18\,SiO_2$$

			Source	Analyst
20	$17\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 16\,H_2O$	$17\,MO = 11.5\,FeO \cdot 5.5\,MnO$	Ottré	Damour
21	$17\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 16\,H_2O$	$17\,MO = 11.5\,FeO \cdot 5.5\,MnO$	Ottré	Damour

G. Compounds of the type

$$\hat{Si}\begin{cases}\bar{R}\\ \bar{R}\\ \bar{R}\end{cases} = 7.5\,R_2O_3 \cdot 6\,SiO_2$$

			Source	Analyst
22	$29\,MO \cdot 2(7.5\,R_2O_3 \cdot 6\,SiO_2) \cdot 12\,H_2O$	$29\,MO = 19.75\,MgO \cdot 8.25\,CaO \cdot 1\,FeO \cdot 15\,R_2O_3 = 14.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Manzoni	Sipöcz

H. Compounds of the type

$$\bar{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \bar{R} = 8\,R_2O_3 \cdot 12\,SiO_2$$

			Source	Analyst
23	$12\,MO \cdot 2(8\,R_2O_3 \cdot 12\,SiO_2) \cdot 12\,H_2O$	$12\,MO = 10\,FeO \cdot 2\,MgO \cdot 16\,R_2O_3 = 11\,Al_2O_3 \cdot 5\,Fe_2O_3$	Natic, Rh. Island	Hermann
24	$24\,MO \cdot 2(8\,Al_2O_3 \cdot 12\,SiO_2) \cdot 14\,H_2O$	$24\,MO = 24\,FeO$	Natic, Rh. Island	Whitney

J. Compounds of the type

$$\hat{Si}\begin{cases}\hat{R}\\ \hat{R}\\ \hat{R}\end{cases} = 9\,R_2O_3 \cdot 6\,SiO_2$$

			Source	Analyst
25	$30\,MO \cdot 2(9\,R_2O_3 \cdot 6\,SiO_2) \cdot 6\,H_2O$	$30\,MO = 21.5\,MgO \cdot 8.5\,CaO \cdot 18\,R_2O_3 = 17.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Ural	G. Wagner
26	$30MO \cdot 2(9R_2O_3 \cdot 6\,SiO_2) \cdot 6\,H_2O$	$30\,MO = 21.5\,MgO \cdot 8.5\,CaO \cdot 18\,R_2O_3 = 17.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Ural	O. Schieffer-decker

K. Compounds of the type

$$\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} = 9\,R_2O_3 \cdot 12\,SiO_2$$

			Source	Analyst
27	$20\,MO \cdot 2(9\,Al_2O_3 \cdot 12\,SiO_2) \cdot 24\,H_2O$	$20\,MO = 15.5\,FeO \cdot 3.5\,MgO \cdot 0.5\,MnO \cdot 0.5\,CaO$	Kaisersberg	v. Foullon
28	$22\,MO \cdot 2(9\,Al_2O_3 \cdot 12\,SiO_2) \cdot 16\,H_2O$	$22\,MO = 21\,FeO \cdot 1\,MgO$	Hetzschen	Schröder
29	$25\,MO \cdot 2(9\,Al_2O_3 \cdot 12\,SiO_2) \cdot 20\,H_2O$	$25\,MO = 19.5\,FeO \cdot 5.5\,MgO$	Kossoibrod	Bonsdorff

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	44.16	25.04	—	16.93	7.98	—	—	5.89	100.00
XIV	43.52	23.89	—	16.81	8.03	—	—	5.63	97.88
Theory	44.16	25.04	—	16.93	7.98	—	—	5.63	100.00
XV	43.34	24.63	—	16.72	8.18	—	—	5.66	98.53

or the general formula

$m\,MO \cdot 2\,(7.5\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	18.95	38.94	2.10	1.89	—	20.80	12.16	5.16	100.00
II*	18.75	39.10	3.24	1.62	—	20.46	12.14	5.35	100.66

or the general formula

$m\,MO \cdot 2\,(8\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	32.89	25.63	18.28	16.45	—	1.82	—	4.93	100.00
XXXIV	32.68	26.38	18.95	16.17	—	1.32	—	4.50	100.00
Theory	28.51	32.30	—	34.20	—	—	—	4.99	100.00
XXXIII	28.27	32.16	—	33.72	—	0.13	—	5.00	99.28

or the general formula

$m\,MO \cdot 2\,(9\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	17.87	44.30	1.99	—	—	21.35	11.81	2.68	100.00
VII†	17.42	44.18	3.53	—	—	20.61	11.95	2.61	100.30
Theory	17.87	44.30	1.99	—	—	21.35	11.81	2.68	100.00
VIII†	17.70	43.60	2.90	—	—	20.90	11.50	2.50	99.10

or the general formula

$m\,MO \cdot 2\,(9\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total
Theory	28.64	36.52	—	22.20	0.71	2.78	0.56	8.59	100.00
II	28.48	36.86	—	21.88	0.97	2.80	0.59	8.09	100.36
Theory	28.15	35.89	—	29.55	—	0.78	—	5.63	100.00
I	28.04	36.19	—	29.79	—	1.25	0.20	5.88	100.35
Theory	27.38	34.91	—	26.69	—	4.18	—	6.84	100.00
XXII	27.48	35.57	—	27.05	0.30	4.29	—	6.95	101.64

* Brandisite † Xanthophyllite

The

The following analyses of the minerals of the

A. $\overline{Si} \cdot \hat{R} \cdot \overline{Si} = 3\,R_2O_3 \cdot 10\,SiO_2$,

B. $\hat{Si} \cdot \hat{R} \cdot \hat{Si} = 3\,R_2O_3 \cdot 12\,SiO_2$,

C. $\hat{R}\left\langle \begin{matrix} \overline{Si} \\ \overline{Si} \\ \overline{Si} \end{matrix} \right. = 3\,R_2O_3 \cdot 15\,SiO_2$,

D. $\hat{R}\left\langle \begin{matrix} \hat{Si} \\ \hat{Si} \\ \hat{Si} \end{matrix} \right. = 3\,R_2O_3 \cdot 18\,SiO_2$,

E. $\ddot{R} \cdot \hat{Si} \cdot \overline{R} = 5\,R_2O_3 \cdot 6\,SiO_2$,

A. Mica of the type

$\overline{Si} \cdot \hat{R} \cdot \overline{Si} = 3\,R_2O_3 \cdot 10\,SiO_2$

				Source
1	$20\,MO \cdot 2\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot 6\,H_2O$	$20\,MO = 16.5\,MgO \cdot 3.5\,K_2O \cdot 6\,R_2O_3 = 4.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	Biotite	Chester, Mass.

B. Mica of the type

$\hat{Si} \cdot \hat{R} \cdot \hat{Si} = 3\,R_2O_3 \cdot 12\,SiO_2$

				Source
2	$6\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2)$	$6\,MO = 1.5\,FeO \cdot 2\,MgO \cdot 2\,K_2O \cdot 0.5\,Na_2O \cdot 6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,V_2O_3$	Roscoe-lite	Colorado
3	$28\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$28\,MO = 23\,MgO \cdot 2\,FeO \cdot 3\,K_2O \cdot 6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Biotite	Moravicza
4	$32\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 2\,H_2O$	$32\,MO = 26.5\,MgO \cdot 2.5\,K_2O \cdot 3\,Na_2O$	,,	Edwards, N.S.

C. Mica of the type

$\hat{R}\left\langle \begin{matrix} \overline{Si} \\ \overline{Si} \\ \overline{Si} \end{matrix} \right. = 3\,R_2O_3 \cdot 15\,SiO_2$

				Source
5	$15\,MO \cdot 2\,(3\,R_2O_3 \cdot 15\,SiO_2) \cdot 20\,H_2O$	$15\,MO = 15\,MgO \cdot 6\,R_2O_3 = 3.5\,Fe_2O_3 \cdot 2.5\,Al_2O_3$	Biotite	Vermont

D. Mica of the type

$\hat{R}\left\langle \begin{matrix} \hat{Si} \\ \hat{Si} \\ \hat{Si} \end{matrix} \right. = 3\,R_2O_3 \cdot 18\,SiO_2$

				Source
6	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 18\,SiO_2) \cdot 6\,H_2O$	$39\,MO = 32\,MgO \cdot 7\,K_2O \cdot 6\,R_2O_3 = 3\,Al_2O_3 \cdot 3\,Fe_2O_3$	Biotite	Herschenberg
7	$47\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 1\,H_2O$	$47\,MO = 3\,FeO \cdot 17\,MnO \cdot 21\,MgO \cdot 3\,CaO \cdot 3\,K_2O$	,,	Pajoberg

Mica Group

Mica group conform to the following types :

F. $\hat{Si} \cdot \bar{R} \cdot \bar{R} \cdot \hat{Si}$ $= 5\,R_2O_3 \cdot 12\,SiO_2$,
G. $\hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si}$ $= 5\,R_2O_3 \cdot 18\,SiO_2$,
H. $\hat{R} \cdot \hat{Si} \cdot \hat{R}$ $= 6\,R_2O_3 \cdot 6\,SiO_2$,
J. $\overline{\overline{Si}} \cdot \hat{R} \cdot \hat{R} \cdot \overline{\overline{Si}}$ $= 6\,R_2O_3 \cdot 10\,SiO_2$,
K. $\hat{Si} \cdot \hat{R} \cdot \hat{R} \cdot \hat{Si}$ $= 6\,R_2O_3 \cdot 12\,SiO_2$,
L. $\overline{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \overline{\overline{Si}}$ $= 6\,R_2O_3 \cdot 16\,SiO_2$,
M. $\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si}$ $= 6\,R_2O_3 \cdot 18\,SiO_2$,
N. $\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R}$ $= 9\,R_2O_3 \cdot 12\,SiO_2$,
O. $\overline{Si} \cdot \hat{R} \cdot \overline{\overline{Si}} \cdot \hat{R} \cdot \dot{Si} \cdot \hat{R} \cdot \overline{Si}$ $= 9\,R_2O_3 \cdot 20\,SiO_2$.

or the general formula

$m\,MO \cdot 2\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Pisani	Theory	39.95	15.28	7.99	—	—	21.97	10.95	—	3.86	100.00
	CLXX	39.55	15.95	7.80	—	—	22.25	10.35	—	4.10	100.00

or the general formula

$m\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Genth	Theory	57.43	20.34	6.00V_2O_3	4.31	—	3.19	7.50	1.23	—	100.00
	—	56.74	19.62	7.78V_2O_3	3.84	—	2.63	8.11	0.94	—	99.66
Rumpf	Theory	40.73	15.87	2.26	4.07	—	26.03	7.98	—	3.06	100.00
	XLIV	40.16	15.79	2.53	4.12	—	26.15	7.64	0.37	3.58	100.34
Crawe	Theory	40.35	17.15	—	—	—	29.70	6.58	5.21	1.01	100.00
	CLI	40.36	16.45	—	—	—	29.55	7.23	4.94	0.95	99.48

or the general formula

$m\,MO \cdot 2\,(3\,R_2O_3 \cdot 15\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Thomson	Theory	50.34	7.13	15.67	—	—	16.79	—	—	10.07	100.00
	CLXXII	49.08	7.28	16.12	—	—	16.96	—	—	10.28	99.72

or the general formula

$m\,MO \cdot 2\,(3\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Bromeis	Theory	43.27	6.13	9.62	—	—	25.64	13.18	—	2.16	100.00
	XXIII	42.89	6.09	10.59	—	—	25.09	13.15	0.36	2.30	100.47
Igelström	Theory	38.63	10.94	—	3.86	3.00	15.01	5.04	21.58MnO	1.94	100.00
	CX	38.50	11.00	—	3.78	3.20	15.01	5.51	21.40MnO	1.60	100.00

E. Micas of the type

$\overline{R} \cdot \hat{Si} \cdot \overline{R} = 5\,R_2O_3 \cdot 6\,SiO_2$

				Source
8	$6.5\,MO \cdot 2\,(5\,Al_2O_3 \cdot 6\,SiO_2)$ $\cdot 6\,H_2O$	$6.5\,MO = 4.5\,CaO \cdot 1.5\,FeO \cdot 0.5\,MgO$	Margarite	Peekskill

F. Micas of the type

$\hat{Si} \cdot \overline{R} \cdot \overline{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 12\,SiO_2$

				Source
9	$3\,MO \cdot 2\,(5\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot 9\,H_2O$	$3\,MO = 1\,FeO \cdot 0.5\,MgO \cdot 1.5\,K_2O$	Pinitoid	Weinheim
10	$5\,MO \cdot 2\,(5\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot 9\,H_2O$	$5\,MO = 1\,MgO \cdot 1.5\,K_2O \cdot 2.5\,Na_2O$	,,	Friebenreuth
11	$6\,MO \cdot 2\,(5\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot 8\,H_2O$	$6\,MO = 2\,MgO \cdot 3.5\,K_2O \cdot 0.5\,Na_2O$	Muscovite	Unionville, Pensylv.
12	$6\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 11\,H_2O$	$6\,MO = 1\,MgO \cdot 0.5\,CaO \cdot 3.5\,K_2O$ $\cdot 1\,Na_2O \cdot 10\,R_2O_3 = 9.5\,Al_2O_3 \cdot 0.5Fe_2O_3$	Pinitoid	Gleichinger Fels
13	$7\,MO \cdot 2\,(5\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot\ 7\,H^2O$	$7\,MO = 4\,FeO \cdot 0.5\,MgO \cdot 2\,K_2O$ $\cdot 0.5\,Na_2O$	,,	Chemnitz
14	$20\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2)$ —	$20\,MO = 9.5\,FeO \cdot 6.5\,MgO \cdot 1.5\,CaO$ $\cdot 2.5Na_2O \cdot 10R_2O_3 = 6\,Al_2O_3 \cdot 4\,Fe_2O_3$	Biotite	Adamello
15	$22\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 48\,H_2O$	$22\,MO = 21\,MgO \cdot 1\,FeO$ $\cdot 10\,R_2O_3 = 8\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	Westchester
16	$23\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 50\,H_2O$	$23\,MO = 22\,MgO \cdot 1\,FeO$ $\cdot 10\,R_2O_3 = 8\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	Westchester
17	$24\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 44\,H_2O$	$24\,MO = 23\,MgO \cdot 0.5\,FeO \cdot 0.5\,NiO$ $\cdot 10\,R_2O_3 = 8.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	,,	Culsagee Mine

G. Micas of the type

$\hat{Si} \cdot \overline{R} \cdot \hat{Si} \cdot \overline{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 18\,SiO_2$

				Source
18	$4\,MO \cdot 2\,(5\,Al_2O_3 \cdot 18\,SiO_2)$ $\cdot 20\,H_2O$	$4\,MO = 1\,FeO \cdot 0.5\,MgO \cdot 2\,K_2O$ $\cdot 0.5\,Na_2O$	Hygro- philite	Rheinpfalz
19	$7\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2)$ $\cdot 6\,H_2O$	$7\,MO = 1\,MnO \cdot 1\,MgO \cdot 5K_2O$ $\cdot 10\,R_2O_3 = 9.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Muscovite	Heidelberg
20	$8\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2)$ $\cdot 12\,H_2O$	$8\,MO = 5.5\,MgO \cdot 0.5\,CaO \cdot 2\,K_2O$ $\cdot 10\,R_2O_3 = 8.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	Gongylite	Yli-Kitka- järvi
21	$25\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2)$ $\cdot 4\,H_2O$	$25MO = 12.5FeO \cdot 5CaO \cdot 0.5MgO \cdot 4.5K_2O$ $\cdot 2.5\,Na_2O$ $\cdot 10\,R_2O_3 = 7\,Fe_2O_3 \cdot 3\,Al_2O_3$	Biotite	Brevik
22	$34\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2)$ $\cdot 12\,H_2O$	$34\,MO = 25\,MgO \cdot 4\,FeO \cdot 5K_2O$ $\cdot 10\,R_2O_3 = 8.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	,,	Karosulik
23	$40\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2)$ $\cdot 2\,H_2O$	$40\,MO = 11.5\,FeO \cdot 23\,MgO \cdot 5\,K_2O$ $\cdot 0.5\,Na_2O$ $\cdot 10\,R_2O_3 = 8\,Al_2O_3 \cdot 2Fe_2O_3$	,,	Tschebarkul
24	$50\,MO \cdot 2\,(5\,Al_2O_3 \cdot 18\,SiO_2)$ $\cdot 34\,H_2O$	$50\,MO = 41.5\,MgO \cdot 8.5\,FeO$	,,	Milbury

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Chatard	Theory	32.32	45.78	—	4.84	11.32	0.90	—	—	4.84	100.00
	XVIII	32.73	46.58	—	5.12	11.04	1.00	—	—	4.49	100.96

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Cohen	Theory	50.44	35.72	—	2.53	—	0.70	4.93	—	5.67	100.00
	III	50.82	35.93	—	2.92	—	0.41	4.13	0.08	5.68	99.99
v. Ammon	Theory	48.68	34.49	—	—	—	1.33	4.78	5.24	5.48	100.00
	IV	49.08	34.75	—	—	—	0.85	5.40	5.30	5.35	100.73
Chatard	Theory	47.30	33.50	—	—	—	2.63	10.81	1.02	4.73	100.00
	C	46.60	32.39	2.54	—	—	2.01	10.39	0.54	4.81	99.28
Hilger	Theory	45.92	30.90	2.55	—	0.89	1.27	10.17	1.98	6.32	100.00
	V	45.24	29.96	3.16	0.32P_2O_5	1.44	1.15	10.13	2.15	6.24	99.79
Knop	Theory	46.26	32.76	—	9.25	—	0.64	6.04	0.99	4.06	100.00
	I	47.77	32.65	—	8.94	—	0.49	5.86	1.50	4.19	101.00
Baltzer	Theory	36.41	15.47	16.19	17.30	2.12	6.57	5.94	—	—	100.00
	LIII	36.43	14.40	16.71	17.40	1.66	6.87	5.54	0.03	—	99.04
König	Theory	33.22	18.81	7.38	1.66	—	19.01	—	—	19.92	100.00
	CXXXVIII	33.35	17.78	7.32	2.11	—	19.26	—	—	19.87	99.69
König	Theory	32.52	18.43	7.23	1.63	—	19.87	—	—	20.32	100.00
	CXL	33.03	17.38	7.41	1.44	—	20.16	—	—	20.90	100.32
Chatard	Theory	33.24	20.01	5.54	0.82	—	21.23	0.86 NiO	—	18.30	100.00
	CXXXII	34.00	20.36	4.91	0.42	—	21.71	0.57 NiO	—	18.50	100.47

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Schwager	Theory	56.08	26.49	—	1.87	—	0.52	4.88	0.80	9.36	100.00
	II	56.64	26.68	—	1.68	0.22	0.29	5.33	0.64	9.13	100.73
Knop	Theory	55.41	24.86	2.05	1.82MnO	—	1.03	12.06	—	2.77	100.00
	I	56.37	24.22	2.09	2.5 MnO	—	0.83	12.61	0.03	2.41	101.06
Thoreld	Theory	55.11	22.12	6.12	—	0.72	5.62	4.80	—	5.51	100.00
	I	55.22	21.80	4.80	0.32MnO	0.77	5.90	4.46	0.45	5.77	99.49
Müller	Theory	39.59	5.60	20.53	16.50	5.13	0.73	7.75	2.84	1.33	100.00
	XCIX	39.38	6.65	19.89	16.43	5.47	0.56	7.86	2.81	1.39	100.44
Kobell	Theory	41.21	16.55	4.58	5.49	—	19.08	8.97	—	4.12	100.00
	CLXXVII	41.00	16.88	4.50	5.05	—	18.86	8.76	—	4.30	99.35
Zellner	Theory	38.72	14.63	5.73	14.85	—	16.50	8.42	0.50	0.65	100.00
	CXX	38.49	14.43	5.44	14.75	—	16.35	8.12	0.53	0.89	99.00
Crossley	Theory	35.62	16.82	—	10.09	—	27.38	—	—	10.09	100.00
	CLXXI	35.74	16.42	—	10.02	—	27.44	—	—	10.30	99.92

H. Micas o

$\hat{R} \cdot \hat{Si} \cdot \hat{R} = 6\ R_2$

25	$1\ MO \cdot 2(6\ Al_2O_3 \cdot 6\ SiO_2) \cdot 2\ H_2O$	$1\ MO = 0.25\ MgO \cdot 0.25\ K_2O \cdot 0.25\ Na_2O \cdot 0.25\ H_2O$	Lesleyite
26	$2\ MO \cdot 2(6\ Al_2O_3 \cdot 6\ SiO_2) \cdot 5\ H_2O$	$2\ MO = 1.75\ K_2O \cdot 0.25\ H_2O$	,,
27	$6\ MO \cdot 2\ (6\ R_2O_3 \cdot 6\ SiO_2) \cdot 7\ H_2O$	$6\ MO = 5\ CaO \cdot 1\ Na_2O \cdot 12\ R_2O_3 = 11.75\ Al_2O_3 \cdot 0.25 Fe_2O_3$	Margarite

J. Micas o

$\overline{Si} \cdot \hat{R} \cdot \hat{R} \cdot \overline{Si} = 6\ R_2$

28	$4\ MO \cdot 2(6\ Al_2O_3 \cdot 10\ SiO_2) \cdot 10\ H_2O$	$4\ MO = 0.5\ CaO \cdot 0.5\ MgO \cdot 1 K_2O \cdot 2\ Na_2O$	Muscovite
29	$4\ MO \cdot 2\ (6\ Al_2O_3 \cdot 10\ SiO_2) \cdot 10\ H_2O$	$4\ MO = 0.5\ CaO \cdot 0.5\ MgO \cdot 1 K_2O \cdot 2\ Na_2O$	,,
30	$4\ MO \cdot 2\ (6\ Al_2O_3 \cdot 10\ SiO_2) \cdot 10\ H_2O$	$4\ MO = 0.5\ CaO \cdot 0.5\ MgO \cdot 1 K_2O \cdot 2\ Na_2O$	,,
31	$4\ MO \cdot 2\ (6\ Al_2O_3 \cdot 10\ SiO_2) \cdot 10\ H_2O$	$4\ MO = 0.5\ CaO \cdot 0.5\ MgO \cdot 1 K_2O \cdot 2\ Na_2O$	,,

K. Micas

$\hat{Si} \cdot \hat{R} \cdot \hat{R} \cdot \hat{Si} = 6\ R_2$

32	$4\ MO \cdot 2\ (6\ R_2O_3 \cdot 12\ SiO_2)$	$4\ MO = 4\ K_2O$ $12\ R_2O_3 = 9.5\ Al_2O_3 \cdot 2.5 Fe_2O_3$	Micarelle
33	$4\ MO \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$4\ MO = 0.5\ CaO \cdot 0.5 MgO \cdot 3 Na_2O$	Paragonite
34	,, ,, ,, ,,	$4\ MO = 1\ K_2O \cdot 3\ Na_2O$	,,
35	$4\ MO \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 9\ H_2O$	$4\ MO = 3.5\ K_2O \cdot 0.5\ Na_2O$	Muscovite
36	,, ,, ,, ,,	$4\ MO = 3.5\ K_2O \cdot 0.5\ Na_2O$	,,
37	,, ,, ,, ,,	$4\ MO = 3.5\ K_2O \cdot 0.5\ Na_2O$	,,
38	,, ,, ,, ,,	$4\ MO = 0.5\ K_2O \cdot 3.5\ Na_2O$	Paragonite
39	,, ,, ,, ,,	$4\ MO = 0.5\ K_2O \cdot 3.5\ Na_2O$	,,
40	,, ,, ,, ,,	$4\ MO = 0.5 MgO \cdot 3 K_2O \cdot 0.5 Na_2O$	Muscovite
41	$4\ MO \cdot 2\ (6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 10\ H_2O$	$4\ MO = 4\ K_2O$	,,
42	$5\ MO \cdot 2(6\ Al_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$5\ MO = 0.5 MgO \cdot 0.5 CaO \cdot 0.5 FeO \cdot 3\ K_2O \cdot 0.5\ Na_2O$	,,

of the general formula
$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Genth	Theory	35.42	60.19	—	—	—	0.51	0.76	1.13	1.99	100.00
	XI	35.68	60.29	0.72	—	—	0.29	0.41	0.96	1.78	100.13
Sharpless	Theory	32.69	55.56	—	—	—	—	7.46	—	4.29	100.00
	V	33.59	55.41	—	—	—	—	7.43	—	4.30	100.73
Smith	Theory	29.65	49.39	1.65	—	11.55	—	—	2.55	5.19	100.00
	IX	30.22	49.67	1.33	—	11.57	Trace	—	2.31	5.12	100.22

or the general formula
$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 10\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Smith & Brush	Theory	41.82	42.65	—	—	0.98	0.69	3.27	4.32	6.27	100.00
	CII	40.29	43.00	1.30	—	1.01	0.62	3.94	5.16	5.00	100.32
,, ,,	Theory	41.82	42.65	—	—	0.98	0.69	3.27	4.32	6.27	100.00
	CIII	39.64	42.40	1.60	—	1.00	0.70	3.94	5.16	5.08	99.52
,, ,,	Theory	41.82	42.65	—	—	0.98	0.69	3.27	4.32	6.27	100.00
	CIV	40.21	41.40	1.30	—	1.11	0.70	3.25	4.26	6.23	99.21
,, ,,	Theory	41.82	42.65	—	—	0.98	0.69	3.27	4.32	6.27	100.00
	CV	40.96	41.40	1.30	—	1.11	0.70	3.25	4.26	6.23	99.21

or the general formula
$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Massalin	Theory	45.21	30.42	12.56	—	—	11.81	—	—	—	100.00
	I	45.00	30.00	12.60	—	—	12.40	—	—	—	100.00
Rammelsberg	Theory	47.34	40.24	—	—	0.92	0.66	—	6.11	4.73	100.00
	II	46.81	40.06	Trace	—	1.26	0.65	Trace	6.40	4.82	100.00
Lemberg	Theory	46.65	39.64	—	—	—	—	3.04	6.01	4.66	100.00
	IV	46.17	40.29	—	—	—	—	3.09	5.53	4.92	100.00
Genth	Theory	45.21	38.42	—	—	—	—	10.32	0.97	5.08	100.00
	XCVII	45.86	37.61	0.59	—	0.31	0.55	10.40	0.80	4.74	100.90
König	Theory	45.21	38.42	—	—	—	—	10.32	0.97	5.08	100.00
	XCVIII	45.73	37.10	1.30	—	—	0.34	10.50	0.88	4.48	100.33
Sauer	Theory	45.21	38.42	—	—	—	—	10.32	0.97	5.08	100.00
	XVIII	45.71	38.64	—	—	—	—	9.53	0.90	5.17	100.00
Cossa	Theory	46.61	39.61	—	—	—	—	1.52	7.02	5.24	100.00
	VII	46.67	39.02	2.01	—	—	—	1.36	6.37	4.91	100.34
,,	Theory	46.61	39.61	—	—	—	—	1.52	7.02	5.24	100.00
	VIII	46.68	39.88	1.06	—	—	—	0.84	6.91	5.08	100.45
König	Theory	45.69	38.75	—	—	—	0.63	8.92	0.98	5.13	100.00
	XC	45.62	35.93	2.93 =	1.87 Al_2O_3	—	0.34	9.40	0.71	4.93	99.86
Delesse	Theory	44.72	38.01	—	—	—	—	11.68	—	5.95	100.00
	XLVIII	45.22	37.85	Trace	—	—	—	11.20	—	5.25	99.52
Blau	Theory	44.93	38.19	—	1.12	0.87	0.62	8.80	0.96	4.49	100.00
	LXXXI	45.57	36.72	0.95	1.28	0.21	0.38	8.81	0.62	5.05	99.93

				Source
43	$5\,MO \cdot 2(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 8\,H_2O$	$5\,MO = 0.5\,MgO \cdot 0.5\,CaO \cdot 0.5\,FeO \cdot 3\,K_2O \cdot 0.5\,Na_2O$	Muscovite	East Indies
44	,, ,, ,, ,,	$5\,MO = 4\,K_2O \cdot 1\,MgO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	,,	Horrsjöberg
45	$7\,MO \cdot 2(6\,Al_2O_3 \cdot 12\,SiO_3) \cdot 12\,H_2O$	$7\,MO = 0.5\,CaO \cdot 2.5\,MgO \cdot 3.5\,K_2O \cdot 0.5\,Na_2O$	,,	Maryland

L. Micas of the type $\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 16\,SiO_2$

				Source
46	$4\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 8\,H_2O$	$4\,MO = 0.5\,FeO \cdot 3\,K_2O \cdot 0.5\,Na_2O$	Killinite	Branchville
47	$5\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 8\,H_2O$	$5\,MO = 1.5\,FeO \cdot 1\,CaO \cdot 0.5\,Li_2O \cdot 2\,K_2O$	,,	Killiney Hill
48	$5\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 9\,H_2O$	$5\,MO = 1\,MgO \cdot 2\,K_2O \cdot 2\,Na_2O$ $12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	Muscovite	Oravicza
49	$6\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 10\,H_2O$	$6\,MO = 0.5\,MgO \cdot 5.5\,K_2O$ $12\,R_2O_3 = 1\,Fe_2O_3 \cdot 11\,Al_2O_3$	,,	Striegau
50	$6\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 22\,H_2O$	$6\,MO = 1.5\,FeO \cdot 0.5\,CaO \cdot 1\,MgO \cdot 3\,K_2O$	Killinite	Killiney Hill
51	$6\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 22\,H_2O$	$6\,MO = 1.5\,FeO \cdot 1.1\,MnO \cdot 0.5\,CaO \cdot 0.5\,MgO \cdot 2.5\,K_2O$	,,	,, ,,
52	$7\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 10\,H_2O$	$7\,MO = 0.5\,FeO \cdot 2.5\,MgO \cdot 4\,K_2O$	Muscovite	Grube Himmelsfürst
53	$7\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 20\,H_2O$	$7\,MO = 1.5\,FeO \cdot 0.5\,CaO \cdot 2\,MgO \cdot 2\,K_2O \cdot 1\,Na_2O$	Hygrophilite	—
54	$8\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 20\,H_2O$	$8\,MO = 2\,FeO \cdot 1\,CaO \cdot 0.5\,MgO \cdot 0.25\,K_2O \cdot 1\,Na_2O$	,,	—
55	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 6\,H_2O$	$12\,MO = 1\,CaO \cdot 3.5\,MgO \cdot 4.5\,K_2O$ $3\,Na_2O$	Paragonite	Fenestrelle
56	$26\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 3\,H_2O$	$26\,MO = 0.5\,CaO \cdot 18.5\,MgO \cdot 7\,K_2O$ $12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	Biotite	Zillerthal
57	$27\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 40\,H_2O$	$27\,MO = 1\,FeO \cdot 0.5\,CaO \cdot 25.5\,MgO$ $12\,R_2O_3 = 8.5\,Al_2O_3 \cdot 3.5\,Fe_2O_3$	,,	Westchester
58	$29\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 60\,H_2O$	$29\,MO = 1.5\,FeO \cdot 27.5\,MgO$ $12\,R_2O_3 = 9\,Al_2O_3 \cdot 3\,Fe_2O_3$	,,	,,
59	$30\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 6\,H_2O$	$30\,MO = 11\,FeO \cdot 12.5\,MgO \cdot 5\,K_20$ $\cdot\,1.5\,Na_2O \cdot 12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	Renchthal
60	$30\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 28\,H_2O$	$30\,MO = 21.5\,FeO \cdot 8.5\,MgO$	,,	Monroe
61	$32\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 32\,H_2O$	$32\,MO = 31.5\,MgO \cdot 0.5\,FeO$ $12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	Calsagee Mine
62	$32\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 64\,H_2O$	$32\,MO = 31.5\,MgO \cdot 0.5\,FeO$ $12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	,,
63	$34\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 60\,H_2O$	$34\,MO = 33.5\,MgO \cdot 0.5\,FeO$ $12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	,,
64	$35\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 34\,H_2O$	$35\,MO = 21.5\,FeO \cdot 1\,CaO \cdot 11.5\,MgO \cdot 1\,K_2O$	,,	Rio de Janeiro

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Sipöcz	Theory	44.93	38.19	—	1.12	0.87	0.62	8.80	0.96	4.49	100.00
	LXXXII	45.71	36.57	1.19	1.07	0.46	0.71	9.22	0.70	4.83	100.67
Igelström	Theory	43.88	34.18	4.87	—	—	1.22	11.46	—	4.39	100.00
	LXXIII	43.41	35.17	4.62	—	—	1.40	10.90	—	4.50	100.00
Chatard	Theory	42.75	36.35	—	—	0.83	2.96	9.77	0.92	6.42	100.00
	XCIII	42.21	34.55	1.03	2.03 Cr_2O_3	0.47	3.13	9.16	0.82	6.77	100.17

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 16\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Dewey	Theory	52.79	33.65	—	0.99	—	—	7.76	0.86	3.95	100.00
	VII	53.47	32.36	0.79	0.42	0.17	0.72 MnO	7.68	0.44	4.07	100.16
Mallet	Theory	52.53	33.49	—	2.95	1.53	—	5.14	0.42 Li_2O	3.94	100.00
	III	52.89	33.24	—	3.27	1.45	—	4.94	0.46 Li_2O	3.67	99.92
Kjerulf	Theory	50.88	27.03	8.47	—	—	1.06	4.98	3.29	4.29	100.00
	XXIV	50.88	26.69	8.48	—	—	1.19	4.52	2.72	4.19	98.67
Riepe	Theory	48.99	28.62	4.08	—	—	0.52	13.20	—	4.59	100.00
	XIX	49.27	28.69	2.89	—	—	0.42	13.91	—	4.77	99.95
Lehunt	Theory	48.03	30.62	—	2.70	0.70	1.00	7.05	—	9.90	100.00
	I	49.08	30.60	—	2.27	0.68	1.08	6.72	—	10.00	100.43
Blythe	Theory	47.98	30.59	1.77 MnO	2.69	0.70	0.50	5.88	—	9.89	100.00
	II	47.93	31.04	1.26 MnO	2.33	0.72	0.46	6.06	—	10.00	99.80
Scheerer	Theory	50.05	31.91	—	0.94	—	2.61	9.80	—	4.69	100.00
	XV	47.84	29.98	2.91	1.12	0.05	2.02	9.48	1.72 TiO_2	4.40	99.52
Killing	Theory	48.36	30.81	—	2.72	0.71	2.02	4.73	1.56	9.07	100.00
	IV	48.60	32.82	—	2.76	0.84	2.37	4.08	1.32	8.83	101.62
Laspeyres	Theory	47.28	30.14	—	3.54	1.38	1.47	5.79	1.53	8.87	100.00
	I	48.42	32.06	—	3.26	1.15	1.72	5.67	1.36	9.02	102.66
Cossa	Theory	47.33	30.17	—	—	1.38	3.45	10.43	4.58	2.66	100.00
	IX	47.96	31.03	—	—	1.07	3.42	10.44	4.08	2.41	100.41
Varren-trapp	Theory	39.54	16.81	13.17	—	0.58	15.24	13.55	—	1.11	100.00
	XLVI	39.85	16.07	13.21	—	0.42	15.60	13.68	—	1.17	100.00
Brush	Theory	37.02	16.72	10.80	1.39	0.54	19.65	—	—	13.88	100.00
	CXXXVII	37.10	17.57	10.54	1.26	0.56	19.65	0.43	—	13.76	100.87
Chatard	Theory	34.25	16.37	8.56	1.93	—	19.62	—	—	19.27	100.00
	CXXXIX	34.40	16.63	8.00	2.11	—	19.30	—	—	19.03	99.47
Killing	Theory	36.73	19.52	6.12	15.23	—	9.57	8.99	1.77	2.07	100.00
	VI	37.67	18.79	6.48	15.28	—	9.72	8.93	1.92	2.33	101.12
Pisani	Theory	34.69	22.11	—	27.96	—	6.14	—	—	9.10	100.00
	CLXIV	34.98	21.88	—	28.44	—	6.24	—	—	9.22	100.76
Cooke	Theory	37.42	19.87	6.23	0.70	—	24.55	—	—	11.33	100.00
	CXXXIII	37.58	19.73	5.95	0.58	—	25.13	—	—	11.09	100.06
Chatard	Theory	33.64	17.88	5.59	0.63	—	22.08	—	—	20.18	100.00
	CXXXI	33.77	17.56	5.61	0.50	—	22.48	—	—	20.30	100.22
König	Theory	33.59	17.85	5.60	0.63	—	23.45	—	—	18.88	100.00
	CXXX	33.93	17.38	5.42	0.50	—	23.43	0.35 NiO	—	19.17	100.18
C.v.Hauer	Theory	32.47	20.70	—	26.17	0.95	7.77	1.59	—	10.35	100.00
	CXXV	32.33	20.47	—	26.25	0.85	7.75	2.02	—	10.33	100.00

M. Micas of the type
$\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 18\,SiO_2$

				Source
65	$5\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 3\,H_2O$	$5\,MO = 0.5\,CaO \cdot 4.5\,K_2O$; $12\,R_2O_3 = 9.5\,Al_2O_3 \cdot 2\,Fe_2O_3 \cdot 0.5\,Mn_2O_3$	Micarelle	—
66	$6\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 18\,H_2O$	$6\,MO = 2\,FeO \cdot 1.5\,MgO \cdot 2\,K_2O \cdot 0.5\,Na_2O$	Killinite	Killiney Hill
67	$6\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 19\,H_2O$	$6\,MO = 1.5\,FeO \cdot 1\,MgO \cdot 3\,K_2O \cdot 0.5\,Na_2O$	,,	Dalkey
68	$7\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 10\,H_2O$	$7\,MO = 0.5\,FeO \cdot 3.5\,MgO \cdot 3\,K_2O$	Muscovite	Tamsweg
69	$26\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 4\,H_2O$	$26\,MO = 12\,FeO \cdot 5.5\,CaO \cdot 5\,K_2O \cdot 3.5\,Na_2O$; $12\,R_2O_3 = 9.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	Biotite	Brevik
70	$29\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2)$	$29\,MO = 23.5\,MgO \cdot 4.5\,K_2O \cdot 1\,Na_2O$; $12\,R_2O_3 = 8.5\,Al_2O_3 \cdot 3.5\,Fe_2O_3$	,,	Laacher See
71	$36\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 86\,H_2O$	$36\,MO = 35.5\,MgO \cdot 0.5\,FeO$; $12\,R_2O_3 = 9.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	,,	Magnet
72	$37\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 12\,H_2O$	$37\,MO = 15.5\,FeO \cdot 2\,MnO \cdot 19.5\,MgO$	,,	Preßburg
73	$39\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O$	$39\,MO = 33\,MgO \cdot 1\,CaO \cdot 5\,K_2O$; $12\,R_2O_3 = 9\,Al_2O_3 \cdot 3\,Fe_2O_3$	,,	Vesuvius

N. Micas of the type
$\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} = 9\,R_2O_3 \cdot 12\,SiO_2$

				Source
74	$12\,MO \cdot 2(9\,Al_2O_3 \cdot 12\,SiO_2) \cdot 12\,H_2O$	$12\,MO = 2\,FeO \cdot 0.5\,MnO \cdot 9.5\,CaO$	Margarite	Tokowaja
75	$29\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 10\,H_2O$	$29\,MO = 1.5\,FeO \cdot 21\,MgO \cdot 1.5\,K_2O \cdot 5\,Na_2O$; $18\,R_2O_3 = 17.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Willcoxite	Shooting Creek
76	$29\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 10\,H_2O$	$29\,MO = 1.5\,FeO \cdot 21\,MgO \cdot 1.5\,K_2O \cdot 5\,Na_2O$; $18\,R_2O_3 = 17.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Cullakenee Mine

O. Micas of the type
$\overline{Si} \cdot \hat{R} \cdot \overline{Si} \cdot \hat{R} \cdot \overline{Si} \cdot \hat{R} \cdot \overline{Si} = 9\,R_2O_3 \cdot 20\,SiO_2$

				Source
77	$4\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 24\,H_2O$	$4\,MO = 0.5\,FeO \cdot 0.5\,MgO \cdot 2.5\,K_2O \cdot 0.5\,CaO$; $18\,R_2O_3 = 17.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Hygrophilite	Nil St. Vincent
78	$6\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 18\,H_2O$	$6\,MO = 5.5\,K_2O \cdot 0.5\,H_2O$; $18\,R_2O_3 = 17\,Al_2O_3 \cdot 1\,Fe_2O_3$	Lesleyite	—
79	$7\,MO \cdot 2(9\,Al_2O_3 \cdot 20\,SiO_2) \cdot 15\,H_2O$	$7\,MO = 2.5\,CaO \cdot 3\,MgO \cdot 1.5\,K_2O$	Muscovite	Dobrawa
80	$8\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 16\,H_2O$	$8\,MO = 1\,MgO \cdot 7\,K_2O$; $18\,R_2O_3 = 16\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	Mt. Leinster Carlow
81	$9\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 16\,H_2O$	$9\,MO = 1\,CaO \cdot 2\,MgO \cdot 4\,K_2O \cdot 2\,Na_2O$; $18\,R_2O_3 = 15.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	,,	Botriphinie
82	$9\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 16\,H_2O$	$9\,MO = 1\,CaO \cdot 2\,MgO \cdot 4\,K_2O \cdot 2\,Na_2O$; $18\,R_2O_3 = 15.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	,,	Vanlup
83	$9\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 12\,H_2O$	$9\,MO = 3\,MgO \cdot 5\,K_2O \cdot 1\,Na_2O$; $18\,R_2O_3 = 17\,Al_2O_3 \cdot 1\,Fe_2O_3$	,	St. Etienne

or the general formula
$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Ficinus	Theory	53.56	24.03	7.93	1.96 Mn_2O_3	0.69	—	10.49	—	1.34	100.00
	II	54.60	23.60	8.60	1.60 Mn_2O_3	0.80	—	11.20	—	1.20	101.60
Galbraith	Theory	52.28	29.63	—	3.48	—	1.45	4.55	0.75	7.84	100.00
	IV	50.45	30.13	—	3.53	—	1.09	4.81	0.95	7.58	98.54
,,	Theory	51.59	29.23	—	2.58	—	0.95	6.73	0.74	8.18	100.00
	V	50.11	29.37	—	2.23	0.34	1.03	6.71	0.60	8.03	98.42
Kobell	Theory	53.71	30.43	—	0.89	—	3.48	7.02	—	4.47	100.00
	XXXIII	52.52	30.88	—	0.80	—	3.82	6.38	—	4.60	99.00
Müller	Theory	36.82	4.32	25.92	14.73	5.25	—	8.02	3.69	1.22	100.00
	C	36.08	4.99	25.98	14.28	5.43	—	7.96	3.68	1.31	99.71
Bromeis	Theory	43.27	17.37	11.22	—	—	18.83	8.07	1.24	—	100.00
	XXII	43.02	16.85	11.63	—	—	19.11	8.60	1.15	—	100.36
König	Theory	33.06	14.84	6.12	0.55	—	21.74	—	—	23.69	100.00
	CXXXV	33.28	14.88	6.36	0.57	—	21.52	—	—	23.90	100.51
C.v.Hauer	Theory	38.26	21.82	—	19.77	—	13.81	2.51 MnO	—	3.83	100.00
	XLV	38.13	21.60	—	19.92	—	13.76	2.61 MnO	—	3.98	100.00
Bromeis	Theory	39.71	16.88	8.82	—	1.02	24.26	8.64	—	0.67	100.00
	LIV	39.75	15.99	8.29	—	0.87	24.49	8.78	—	0.75	98.92

or the general formula
$m\,MO \cdot 2\,(9\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Jewrechow	Theory	34.26	43.68	—	3.42	12.67	0.84 MnO	—	—	5.13	100.00
	XV	34.02	43.33	—	3.02	13.11	1.05 MnO	—	—	5.34	99.87
König	Theory	29.48	36.56	1.64	2.22	—	17.20	2.88	6.34	3.68	100.00
	I	28.96	37.49	1.26	2.46	—	17.35	2.46	6.73	4.00	100.69
,,	Theory	29.48	36.56	1.64	2.22	—	17.20	2.88	6.34	3.68	100.00
	II	29.50	37.56	1.40	2.42	—	17.20	2.42	6.24	3.32	100.02

or the general formula
$m\,MO \cdot 2\,(9\,R_2O_3 \cdot 20\,SiO_2) \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Renard	Theory	47.33	35.19	1.58	1.41	0.55	0.79	4.63	—	8.52	100.00
	III	47.02	34.82	2.57	0.68	0.20	0.52	4.60	0.18	8.35	98.94
Roepper	Theory	46.66	33.71	3.11	—	—	—	10.05	—	6.47	100.00
	VIII	47.02	33.27	2.84	—	—	—	9.97	—	6.71	99.79
Böricky	Theory	48.91	37.42	—	—	2.85	2.44	2.87	—	5.51	100.00
	XXX	48.74	37.96	—	—	2.63	2.41	3.07	—	5.45	100.26
Haughton	Theory	44.96	30.57	5.99	—	—	0.75	12.33	—	5.40	100.00
	LVIII	44.64	30.18	6.35	—	—	0.72	12.40	—	5.32	99.61
Heddle	Theory	45.24	29.80	7.54	—	1.06	1.51	7.09	2.34	5.43	100.00
	LI	45.10	29.90	7.87	0.03 MnO	0.62	0.72	7.84	2.56	5.51	100.15
,,	Theory	45.24	29.80	7.54	—	1.06	1.51	7.09	2.34	5.43	100.00
	LIV	45.43	29.65	8.33	0.02 MnO	0.79	1.70	6.94	2.27	5.29	100.42
Delesse	Theory	46.67	33.71	3.12	—	—	1.94	9.14	1.21	4.21	100.00
	XLVII	46.23	33.03	3.48	—	—	2.10	8.87	1.45	4.12	99.28

				Source
84	$10\,MO \cdot 2(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 4\,H_2O$	$10\,MO = 4\,K_2O \cdot 3.5\,Na_2O \cdot 2.5\,MgO$ $18\,R_2O_3 = 17.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Muscovite	Zillertal
85	$14\,MO \cdot 2(9\,Al_2O_3 \cdot 20\,SiO_2) \cdot 11\,H_2O$	$14\,MO = 1.5\,FeO \cdot 2\,BaO \cdot 0.5\,CaO \cdot 4\,MgO \cdot 4.5\,K_2O \cdot 1.5\,Na_2O$	,,	Pfitschtal
86	$14\,MO \cdot 2(9\,Al_2O_3 \cdot 20\,SiO)_2 \cdot 11\,H_2O$	$14\,MO = 1.5\,FeO \cdot 2\,BaO \cdot 0.5\,CaO \cdot 4\,MgO \cdot 4.5\,K_2O \cdot 1.5\,Na_2O$	,,	,,

New Formulæ for the

The following analyses of the minerals

A. $\bar{Si} \cdot \hat{R} \cdot \bar{Si} = 3\,R_2O_3 \cdot 10\,SiO_2$,

B. $\hat{Si} \cdot \hat{R} \cdot \hat{Si} = 3\,R_2O_3 \cdot 12\,SiO_2$,

C. $\hat{R}\begin{cases}\bar{Si}\\ \bar{Si}\\ \bar{Si}\end{cases} = 3\,R_2O_3 \cdot 15\,SiO_2$,

D. $\bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 12\,SiO_2$,

E. $\hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 18\,SiO_2$,

A. Scapolites of the type

$\bar{Si} \cdot \hat{R} \cdot \bar{Si} = 3\,R_2O_3 \cdot 10\,SiO_2$

			Source	Analyst
1	$6\,MO \cdot 2(3\,R_2O_3 \cdot 10\,SiO_2) \cdot 6\,H_2O$	$6\,MO = 3\,MgO \cdot 2.5\,K_2O \cdot 0.5\,H_2O$ $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	Algerite Franklin N.J.	Crossley
2	$9\,MO \cdot 2(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 2\,H_2O$	$9\,MO = 4.25\,CaO \cdot 4.25\,Na_2O \cdot 0.5\,H_2O$	St. Lawrence Co., N.S.	Rammelsberg
3	$9\,MO \cdot 2(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 0.5\,H_2O$	$9\,MO = 5.75\,CaO \cdot 2.75\,Na_2O \cdot 0.25\,MgO \cdot 0.25\,K_2O$	Arendal	Wolff
4	$9\,MO \cdot 2(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 4\,H_2O$	$9\,MO = 6\,CaO \cdot 2.25\,Na_2O \cdot 0.25\,K_2O \cdot 0.5\,H_2O$	Arendal	Damour
5	$11\,MO \cdot 2(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 2.5\,H_2O$	$11\,MO = 7.75\,CaO \cdot 1.5\,Na_2O \cdot 0.25\,K_2O \cdot 1.5\,MgO$	Malsjö	G. v. Rath
6	$12\,MO \cdot 8(3\,R_2O_3 \cdot 10\,SiO_2) \cdot 40\,H_2O \cdot 4\,CaCO_3$	$12\,MO = 10\,K_2O \cdot 2\,MgO \cdot 24\,R_2O_3 = 23\,Al_2O_3 \cdot 1\,Fe_2O_3$	Algerite Franklin N.J.	Hunt
7	$23\,MO \cdot 8(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 2\,H_2O \cdot 3\,CaCO_3$	$23\,MO = 12\,CaO \cdot 10\,Na_2O \cdot 1\,K_2O$	Gulsjö	Hermann
8	$22\,MO \cdot 8(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 26\,H_2O \cdot 4\,CaCO_3)$	$22\,MO = 12\,MgO \cdot 10\,K_2O \cdot 24\,R_2O_3 = 23\,Al_2O_3 \cdot 1\,Fe_2O_3$	Algerite Franklin N.J.	Crossley
9	$36\,MO \cdot 8(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 12\,H_2O \cdot 1\,CaCO_3$	$36\,MO = 22\,CaO \cdot 9\,Na_2O \cdot 2\,K_2O \cdot 3\,MgO$	Malsjö	G. v. Rath
10	$30\,MO \cdot 8(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 2\,H_2O \cdot 1\,CaSO_4$	$30\,MO = 20\,CaO \cdot 10\,Na_2O$	Kupfermine	Lacroix

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Schafhäutl	Theory	47.72	35.49	1.59	—	—	1.98	7.47	4.32	1.43	100.00
	XXXVI	47.05	34.90	1.50	—	—	1.95	7.96	4.07	1.45	98.88
Rammelsberg	Theory	43.39	33.19	5.51 BaO	1.95	0.56	2.88	7.28	1.68	3.56	100.00
	XL	43.09	32.79	5.91 BaO	1.85	0.23	2.90	7.61	1.42	4.26	100.35
Rammelsberg	Theory	43.39	33.19	5.51 BaO	1.95	0.56	2.88	7.28	1.68	3.56	100.00
	XLI	42.90	32.40	5.82 BaO	2.40	0.80	2.87	7.47	1.73	3.02	99.41

Scapolite Group

of this group conform to the following formulæ:

F. $\bar{Si} \cdot \bar{R} . \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \bar{Si} = 5\,R_2O_3 \cdot 22\,SiO_2$,

G. $\hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} = 6\,R_2O_3 \cdot 12\,SiO_2$,

H. $\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 16\,SiO_2$,

J. $\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 18\,SiO_2$,

K. $\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 22\,SiO_2$,

L. $\bar{Si} \cdot \hat{R} \cdot \bar{Si} \cdot \hat{R} \cdot \bar{Si} \cdot \hat{R} \cdot \bar{Si} = 9\,R_2O_3 \cdot 20\,SiO_2$.

or the general formulæ

(a) $m\,MO \cdot 2\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot n\,H_2O$,

(b) $m\,MO \cdot 8\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot n\,H_2O \cdot p\,CaCO_3$ (or $p\,CaSO_4$).

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	52.21	25.52	1.74	—	5.22	—	10.22	—	5.09	—	—	—	—	100.00
LXXXIa	52.00	25.42	1.54	—	5.39	—	10.38	—	5.27	—	—	—	—	100.00
Theory	50.88	25.95	—	—	—	10.09	—	11.17	1.91	—	—	—	—	100.00
XCII	50.73	25.40	—	—	—	10.24	—	11.09	1.96	—	—	—	0.09	99.60
Theory	51.14	26.07	—	—	0.43	13.75	1.00	7.26	0.38	—	—	—	—	100.00
XXX	50.91	25.81	0.75	—	0.58	13.34	0.85	7.09	0.41	—	—	—	—	99.74
Theory	50.17	25.58	—	—	—	14.05	0.98	5.83	3.39	—	—	—	—	100.00
XXXVI	50.30	25.08	—	—	—	14.08	1.01	5.98	3.25	—	—	—	—	99.70
Theory	48.63	24.81	—	—	2.43	17.59	0.95	3.77	1.82	—	—	—	—	100.00
XLII	47.24	24.69	Trace	—	2.18	16.84	0.85	3.55	1.72	—	—	—	—	98.07
Theory	50.81	24.84	1.69	—	0.85	2.37	9.95	—	—	—	—	1.86	—	100.00
LXXX	49.82	24.91	1.85	—	1.15	2.20	10.21	Trace	7.57	—	—	1.74	—	99.45
Theory	53.52	27.29	—	—	—	9.36	1.05	6.91	0.40	—	—	1.47	—	100.00
XLV	52.94	27.64	—	0.30	0.25 MnO	9.10	0.54	6.89	0.66	—	—	1.50	—	99.72
Theory	50.03	24.45	1.68	—	5.00	—	9.80	—	4.87	—	4.17	—	—	100.00
LXXXI	49·96	24.41	1.48	—	5.18	—	9.97	—	5.06	—	4.21	—	—	100.27
Theory	49.68	25.33	—	—	1.24	12.75	1.95	5.77	2.24	—	1.04	—	—	100.00
XLI	49.36	25.33	—	—	1.05	12.47	1.51	5.81	2.42	—	1.35	—	—	99.35
Theory	52.41	26.72	—	—	—	12.84	—	6.77	0.39	0.87 SO_3	—	—	—	100.00
CXV	52.62	26.42	Trace	—	—	13.11	0.45	6.62	0.43	0.79 SO_3	—	—	0.10	100.54

B. Scapolites of the type

$$\hat{Si} \cdot \hat{R} \cdot \hat{Si} = 3\,R_2O_3 \cdot 12\,SiO_2$$

			Source	Analyst
11	$9\,MO \cdot 2(3\,Al_2O_3 \cdot 12\,SiO_2)$	$9\,MO = 4.25\,CaO \cdot 4.25\,Na_2O \cdot 0.5\,K_2O$	Mizzonite	Rath
12	$9\,MO \cdot 2(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 1\,H_2O$	$9\,MO = 4.25\,CaO \cdot 1.75\,K_2O \cdot 1.5\,Na_2O \cdot 1\,MgO \cdot 0.5\,H_2O$	Dipyre from Pouzac	H. Schulz
13	$15\,MO \cdot 4(3\,AlO_3 \cdot 12\,SiO_2) \cdot 3\,NaCl$	$15\,MO = 9\,CaO \cdot 5.5\,Na_2O \cdot 0.5\,K_2O$	St.Lawrence Co., N.S.	Lemberg

C. Scapolites of the type

$$\hat{R}\begin{cases}\bar{Si}\\ \bar{Si}\\ \bar{Si}\end{cases} = 3\,R_2O_3 \cdot 15\,SiO_2$$

			Source	Analyst
14	$8\,MO \cdot 2(3\,Al_2O_3 \cdot 15\,SiO_2)$	$8\,MO = 4.5Na_2O \cdot 2.5\,CaO \cdot 0.5\,MgO \cdot 0.5\,K_2O$	Marialite, Pianura	G. v. Rath
15	$10\,MO \cdot 2(3\,Al_2O_3 \cdot 15\,SiO_2) \cdot 4\,H_2O$	$10\,MO = 5.5\,MgO \cdot 3\,K_2O \cdot 0.75\,FeO \cdot 0.25\,Na_2O \cdot 0.5\,CaO$	Couseranite, Pouzac	Pisani

D. Scapolites of the type

$$\bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 12\,SiO_2$$

			Source	Analyst
16	$10\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2)$	$10\,MO = 10\,CaO$	Stansvik	Lagus Olckonen
17	$10\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2) \cdot 2\,H_2O$	$10\,MO = 9\,CaO \cdot 1\,Na_2O$	Clay Co., N.C.	Berkley
18	$11\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2) \cdot 2\,H_2O$	$11\,MO = 10\,CaO \cdot 0.5\,K_2O \cdot 0.5\,Na_2O$	Pargas	Wolff
19	$11\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2) \cdot 17\,H_2O$	$11\,MO = 4\,MgO \cdot 3\,CaO \cdot 3\,K_2O \cdot 1\,Na_2O$	Wilsonite Bathurst, Canada	Selkmann
20	$12\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2)$	$12\,MO = 12\,CaO$	Stansvik	Lagus Olckonen
21	$14\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2)$	$14\,MO = 12\,CaO \cdot 1.5\,Na_2O \cdot 0.5\,K_2O$	Ersbyite, Pargas	N. Nordenskiöld
22	$15\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2)$	$15\,MO = 13\,CaO \cdot 2\,Na_2O$	Baikalsee	Hermann
23	$15\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2)$	$15\,MO = 13\,CaO \cdot 1\,MgO \cdot 0.5\,K_2O \cdot 0.5\,Na_2O$	Mejonite from Vesuvius	G. v. Rath
24	$18\,MO \cdot 2(5\,Al_2O_3 \cdot 12\,SiO_2) \cdot 14\,H_2O$	$18\,MO = 15.5\,CaO \cdot 2.5\,MgO \cdot 10\,R_2O_3 = 8.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	Atheriastite, Arendal	Berlin

or the general formulae

(a) m MO · 2 (3 R_2O_3 · 12 SiO_2) · n H_2O,
(b) m MO · 4 (3 R_2O_3 · 12 SiO_2) · n NaCl.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	55.38	23.52	—	—	—	9.15	1.82	10.13	—	—	—	—	—	100.00
XVI	54.70	23.80	—	—	0.22	8.77	2.14	9.83	0.13	—	—	—	—	99.59
Theory	55.08	23.41	—	—	1.53	9.10	6.29	3.56	1.03	—	—	—	—	100.00
XXIII	53.97	23.68	—	—	1.40	8.76	6.43	3.55	0.98	—	—	—	—	98.77
Theory	55.69	23.67	—	—	—	9.75	0.91	6.59	—	3.39	—	—	—	100.00
XCIV	55.04	23.62	—	—	—	9.38	0.73	6.29	0.28	3.69	—	—	—	99.03

or the general formula

m MO · 2 (3 R_2O_3 · 15 SiO_2) · n H_2O.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	62.11	21.12	—	—	0.69	4.83	1.62	9.63	—	—	—	—	—	100.00
XVIII	62.72	21.82	—	—	0.31	4.62	1.15	9.37	—	—	—	—	—	100.00
Theory	58.37	19.85	—	1.75	7.14	0.90	9.15	0.50	2.34	—	—	—	—	100.00
XXV	58,33	20.20	—	1.90	7.20	0.99	8.82	0.76	2.35	—	—	—	—	100.55

or the general formula

m MO · 2 (5 R_2O_3 · 12 SiO_2) · n H_2O.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	47.68	33.77	—	—	—	18.55	—	—	—	—	—	—	—	100.00
LXVIII	47.60	33.50	—	—	—	17.20	—	—	—	—	—	—	—	98.30
Theory	47.03	33.31	—	—	—	16.46	—	2.02	1.18	—	—	—	—	100.00
LXXVIII	47.54	34.03	—	—	—	17.23	—	1.82	1.02	—	—	—	—	101.64
Theory	45.95	32.55	—	—	—	17.87	1.50	0.99	1.14	—	—	—	—	100.00
LIX	45.10	32.76	—	—	—	17.84	0.68	0.76	1.04	—	—	—	—	98.18
Theory	41.88	29.66	—	—	4.66	4.89	8.20	1.80	8.91	—	—	—	—	100.00
CXIII	41.26	30.31	—	—	4.20	5.34	7.43	1.97	8.83	—	—	—	—	99.34
Theory	45.98	32.56	—	—	—	21.46	—	—	—	—	—	—	—	100.00
LXIX	45.60	32.60	—	—	—	23.40	—	—	—	—	—	—	—	101.60
Theory	44.02	31.17	—	—	—	20.54	1.43	2.84	—	—	—	—	—	100.00
LVII	44.26	30.37	—	—	0.15	20.17	1.15	2.75	—	—	—	—	—	98.85
Theory	43.48	30.80	—	—	—	21.98	—	3.74	—	—	—	—	—	100.00
LXXVa	43.35	30.52	0.95	—	—	21.59	—	3.74	—	—	—	—	—	100.15
Theory	43.56	30.85	—	—	1.21	22.02	1.42	0.94	—	—	—	—	—	100.00
XIII	42.55	30.89	0.41	—	0.83	21.41	0.93	1.25	—	—	—	—	—	98.46
Theory	38.23	23.02	6.37	—	2.65	23.04	—	—	6.69	—	—	—	—	100.00
XXXVIII	38.00	24.10	5·60	—	2.80	22.64	—	—	6.95	—	—	—	—	100.09

E. Scapolites of the type
$\hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 18\,SiO_2$

			Source	Analyst
25	$14\,MO \cdot 2(5\,R_2O_3 \cdot 18\,SiO_2)$	$14\,MO = 9\,CaO \cdot 4.5\,Na_2O \cdot 0.5\,K_2O$	Malsjö	Sipöcz
26	$14\,MO \cdot 2(5\,R_2O_3 \cdot 18\,SiO_2) \cdot 14\,H_2O$	$14\,MO = 6\,CaO \cdot 3\,K_2O \cdot 3\,MgO \cdot 1\,Na_2O \cdot 1\,FeO$; $10\,R_2O_3 = 9\,Al_2O_3 \cdot 1\,Fe_2O_3$	Tiree	F. Heddle
27	$32\,MO \cdot 2(5\,Al_2O_3 \cdot 18\,SiO_2) \cdot 10\,H_2O$	$32\,MO = 31\,CaO \cdot 1\,MgO$	Storgard	Nordenskiöld
28	$8\,MO \cdot 2(5\,R_2O_3 \cdot 18\,SiO_2) \cdot 10\,H_2O \cdot 3\,CaCO_3)$	$8\,MO = 3.5\,K_2O \cdot 2.5\,CaO \cdot 2\,MgO$ $10\,R_2O_3 = 9.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Bolton, Mass.	G. v. Rath

F. Scapolites of the type
$\bar{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \bar{Si} = 5\,R_2O_3 \cdot 22\,SiO_2$

			Source	Analyst
29	$12\,MO \cdot 2(5\,R_2O_3 \cdot 22\,SiO_2) \cdot 10\,H_2O$	$12\,MO = 6.5\,Na_2O \cdot 5\,CaO \cdot 0.5\,MgO$ $10\,R_2O_3 = 9\,Al_2O_3 \cdot 1\,Fe_2O_3$	Coquimbo	Jannetaz
30	$15\,MO \cdot 2(5\,Al_2O_3 \cdot 22\,SiO_2)$	$15\,MO = 3\,MgO \cdot 6\,CaO \cdot 6\,Na_2O$	Bamle	Vogt

G. Scapolites of the type
$\hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} = 6\,R_2O_3 \cdot 12\,SiO_2$

			Source	Analyst
31	$11\,MO \cdot 2(6\,Al_2O_3 \cdot 12\,SiO_2)$	$11\,MO = 11\,CaO$	Helsingfors	Wilk
32	$11\,MO \cdot 2(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 2\,H_2O$	$11\,MO = 11\,CaO$	Pargas	Nordenskiöld

H. Scapolites of the type
$\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 16\,SiO_2$

			Source	Analyst
33	$9\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 2\,H_2O$	$9\,MO = 6\,CaO \cdot 3\,Na_2O \cdot 12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Petteby	Hartwall
34	$10\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 12\,H_2O$	$10\,MO = 4.5\,MgO \cdot 4\,K_2O \cdot 1\,CaO \cdot 0.5\,Na_2O$	Bathurst, Canada	Hunt
35	$13\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2)$	$13\,MO = 10.5\,CaO \cdot 1.5\,Na_2O \cdot 0.5\,K_2O \cdot 0.5H_2O$; $12R_2O_3 = 11.5Al_2O_3 \cdot 0.5Fe_2O_3$	Diana, Lewis Co., N.S.	Hermann
36	$13\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 1\,H_2O$	$13\,MO = 11\,CaO \cdot 2\,Na_2O$	Ersby	Hartwall Herdberg
37	$14\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 21\,H_2O$	$14\,MO = 5\,CaO \cdot 4\,MgO \cdot 4\,K_2O \cdot 1\,Na_2O$	Bathurst, Canada	Hunt
38	$17\,MO \cdot 2(6\,Al_2O_3 \cdot 16\,SiO_2) \cdot 1\,H_2O$	$17\,MO = 14.5\,CaO \cdot 2\,Na_2O \cdot 0.5\,K_2O$	Laacher See	Rath
39	$18\,MO \cdot 2(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 3\,H_2O$	$18\,MO = 15.5\,CaO \cdot 1.5\,Na_2O \cdot 1\,MgO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Bolton, Mass.	G. v. Rath

or the general formulæ

(a) m MO · 2 (5 R_2O_3 · 18 SiO_2) · n H_2O,

(b) m MO · 2 (5 R_2O_3 · 18 SiO_2) · n H_2O. p $CaCO_3$.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	53.86	25.44	—	—	—	12.57	1.17	6.96	—	—	—	—	—	100.00
XLIII	52.48	25.56	—	0.39	—	12.44	0.79	6.52	0.61	0.58 SO_3	—	0.14	0.27	99.78
Theory	49.52	21.05	3.67	1.65	2.75	7.70	6.47	1.42	5.77	—	—	—	—	100.00
XXIX	48.92	22.10	3.16	1.51	2.77	7.75	6.06	1.28	5.69	0.54 MnO	—	—	—	99.78
Theory	42.06	19.86	—	—	0.78	33.80	—	—	3.50	—	—	—	—	100.00
LV	41.25	20.36	—	—	0.54	33.58	—	—	3.32	—	—	—	—	99.05
Theory	50.97	22.87	1.89	—	1.89	3.30	7.76	—	4.25	—	7.07	—	—	100.00
CVI	49.99	23.01	1.64	—	1.73	3.35	7.09	0.35	4.23	—	7.80	—	—	99.19

or the general formula

m MO · 2 (5 R_2O_3 · 22 SiO_2) · n H_2O.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	57.38	19.95	3.48	—	0.43	6.09	—	8.76	3.91	—	—	—	—	100.00
LXXVII	57.40	19.60	3.40	—	0.40	6.20	Trace	8.80	3.41	—	—	—	—	99.21
Theory	58.82	22.73	—	—	2.67	7.49	—	8.29	—	—	—	—	—	100.00
XXXIX	59.66	22.65	—	—	2.60	7.32	—	8.13	—	—	—	—	—	100.36

or the general formula

m MO · 2 (6 R_2O_3 · 12 SiO_2) · n H_2O.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	43.90	37.32	—	—	—	18.78	—	—	—	—	—	—	—	100.00
LXX	43.63	36.93	—	—	—	18.37	—	—	—	—	—	—	—	98.93
Theory	43.43	36.91	—	—	—	18.57	—	—	1.09	—	—	—	—	100.00
LIII	43.83	35.43	—	—	—	18.96	—	—	1.03	—	—	—	—	99.25

or the general formula

m MO · 2 (6 R_2O_3 · 16 SiO_2) · n H_2O.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	51.46	31.44	2.15	—	—	9.01	—	4.98	0.96	—	—	—	—	100.00
LXVII	51.34	32.27	1.91	—	—	9.33	—	5.12	1.00	—	—	—	—	100.97
Theory	47.97	30.58	—	—	4.50	1.40	9.39	0.77	5.39	—	—	—	—	100.00
CXII	47.60	31.20	—	—	4.19	0.95	9.30	0.88	5.43	—	—	—	—	99.55
Theory	49.10	30.00	2.05	—	—	15.04	1.20	2.38	0.22	—	—	—	—	100.00
LXXXVI	47.94	30.02	2.60	0.26 MnO	—	14.41	0.73	2.20	0.31	—	—	—	—	98.47
Theory	49.20	31.37	—	—	—	15.79	—	3.18	0.46	—	—	—	—	100.00
LXV	48.87	31.05	—	—	—	15.94	—	3.25	0.61	—	—	—	—	99.62
Theory	43.64	27.82	—	—	3.63	6.36	8.55	1.41	8.59	—	—	—	—	100.00
CXI	43.55	27.94	0.20	—	3.81	6.50	8.37	1.45	8.61	—	—	—	—	100.43
Theory	46.32	29.53	—	—	—	19.59	1.14	2.99	0.43	—	—	—	—	100.00
I	45.13	29.83	—	—	0.13	18.98	1.40	2.73	0.41	—	—	—	—	98.61
Theory	45.09	26.35	3.76	—	0.94	20.39	—	2.18	1.29	—	—	—	—	100.00
CV	44.40	25.52	3.79	—	1.01	20.18	0.51	2.09	1.24	—	—	—	—	98.74

J. Scapolites of the type

$\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 18\,SiO_2$

			Source	Analyst
40	$2\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 6\,H_2O$	$2\,MO = 1.5\,Na_2O \cdot 0.5\,H_2O$	St. Lawrence Co., N.S.	Rammelsberg
41	$3\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O$	$3\,MO = 1\,CaO \cdot 1\,Na_2O \cdot 0.5\,MgO \cdot 0.5\,K_2O$	Bolton, Mass.	Hermann
42	$14\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 1\,H_2O$	$14\,MO = 10\,CaO \cdot 2.5\,Na_2O \cdot 0.5\,FeO \cdot 0.5\,K_2O \cdot 0.5\,MgO$	Boxborough	Becke
43	$14\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 4\,H_2O$	$14\,MO = 8\,CaO \cdot 3.5\,MgO \cdot 2\,Na_2O \cdot 0.5\,K_2O$	Glaukolite Baikalsee	Bergemann
44	$14\,MO \cdot 2(6Al_2O_3 \cdot 18\,SiO_2) \cdot 4\,H_2O$	$14\,MO = 8.5\,CaO \cdot 2.5\,MgO \cdot 2\,Na_2O \cdot 0.5\,MnO \cdot 0.5\,K_2O$	,,	Giwartowsky
45	$15\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O$	$15\,MO = 11\,CaO \cdot 4\,Na_2O$	Obernzell bei Passau	Fuchs
46	$17\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O$	$17\,MO = 12\,CaO \cdot 3\,Na_2O \cdot 1.5\,MgO \cdot 0.5\,K_2O$	Bolton, Mass.	Wolff
47	$18\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O$	$18\,MO = 13.5CaO \cdot 3.5\,Na_2O \cdot 1\,MgO$ $12\,R_2O_3 = 11.5Al_2O_3 \cdot 0.5Fe_2O_3$	Hirvensalo	,,
48	$18\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 4\,H_2O$	$18\,MO = 14\,CaO \cdot 3.5\,Na_2O \cdot 0.5\,MgO$	Drothem	Berg
49	$18\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 13\,H_2O$	$18\,MO = 15.5\,CaO \cdot 2.5\,Na_2O$	Bolton, Mass.	Thomson
50	$19\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 4\,H_2O$	$19\,MO = 14.5\,CaO \cdot 2.5\,Na_2O \cdot 1.5\,MgO \cdot 0.5\,K_2O$	Bucks Co., Pa.	Leeds
51	$19\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 7\,H_2O$	$19\,MO = 11\,CaO \cdot 4\,MgO \cdot 2\,Na_2O \cdot 2\,K_2O$	Perth, Canada	Hunt
52	$20\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2)$	$20\,MO = 14\,CaO \cdot 6\,Na_2O$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Bolton, Mass.	Wurtz
53	$20\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 1\,H_2O$	$20\,MO = 14\,CaO \cdot 5.5\,Na_2O \cdot 0.5\,K_2O$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Arendal	G. v. Rath
54	$22\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O$	$22\,MO = 18\,CaO \cdot 2\,Na_2O \cdot 1.5\,MgO \cdot 0.5\,K_2O$; $12\,R_2O_3 = 11Al_2O_3 \cdot 1\,Fe_2O_3$	Bolton, Mass.	,,
55	$11\,MO \cdot 2(6\,R_2O_3 \cdot 18\,SiO_2) \cdot 3\,Na_2CO_3$	$11\,MO = 10\,CaO \cdot 0.5\,MgO \cdot 0.5\,K_2O$ $12\,R_2O_3 = 11.25\,Al_2O_3 \cdot 0.75\,Fe_2O_3$	Hesselkulla	Hermann
56	$12\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 6\,NaCl$	$12\,MO = 12\,CaO$	Obernzell bei Passau	Fuchs
57	$15\,MO \cdot 2(6\,Al_2O_3 \cdot 18\,SiO_2) \cdot 2\,H_2O \cdot 1\,NaCl$	$15\,MO = 12\,CaO \cdot 2.5\,Na_2O \cdot 0.5\,K_2O$	Ersby	Lemberg

or the general formulæ

(a) m MO · 2 (6 R_2O_3 · 18 SiO_2) · n H_2O,

(b) m MO · 2 (6 R_2O_3 · 18 SiO_2) · p Na_2CO_3 (or p · NaCl).

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	60.10	34.05	—	—	—	—	—	2.59	3.26	—	—	—	—	100.00
XCIII	59.29	34.78	—	—	0.07	0.11	—	2.31	3.31	—	—	—	0.20	100.07
Theory	52.56	29.79	—	—	0.49	13.63	1.14	1.51	0.88	—	—	—	—	100.00
CIII	51.68	29.30	—	—	0.78	13.51	0.94	1.46	0.82	0.15MnO	—	—	—	99.80
Theory	51.19	29.00	—	0.85	0.47	13.27	1.11	3.68	0.43	—	—	—	—	100.00
CVIII	50.53	29.31	--	0.49	0.46	13.37	1.23	3.91	0.54	—	—	—	0.21	100.05
Theory	51.25	29.03	—	—	3.32	10.63	1.11	2.94	1.72	—	—	—	—	100.00
LXXII	50.58	27.60	0.86Mn_2O_3	0.10	3.72	10.27	1.27	2.97	1.73	—	—	—	—	99.11
Theory	50.96	28.88	—	0.84MnO	2.36	11.23	1.10	2.93	1.70	—	—	—	—	100.00
LXXIII	50.49	28.12	0.40 FeO	0.60MnO	2.68	11.31	1.00	3.10	1.79	—	—	—	—	99.49
Theory	50.42	28.57	—	—	—	14.38	—	5.79	0.84	—	—	—	—	100.00
II	49.30	27.90	—	—	—	14.42	—	5.46	0.90	—	—	—	—	97.98
Theory	49.26	27.92	—	—	1.37	15.33	1.07	4.24	0.81	—	—	—	—	100.00
C	48.79	28.16	0.32	—	1.29	15.02	0.54	4.52	0.74	—	—	—	—	99.38
Theory	48.41	26.29	1.79	—	0.90	16.94	—	4.86	0.81	—	—	—	—	100.00
LII	48.15	25.38	1.48	—	0.84	16.63	0.12	4.91	0.85	—	—	—	—	98.36
Theory	48.25	27.34	—	—	0.45	17.51	—	4.85	1.60	—	—	—	—	100.00
XLVII	46.35	26.34	0.32	—	0.54	17.00	0.32	4.71	1.60	0.99 Residue	—	—	—	98.17
Theory	46.54	26.37	—	—	—	18.71	—	3.34	5.04	—	—	—	—	100.00
XCIX	46.30	26.48	—	—	—	18.64	—	3.64	5.04	—	—	—	—	100.08
Theory	47.68	27.02	—	—	1.32	17.93	1.04	3.42	1.59	—	—	—	—	100.00
LXXXV	47.47	27.51	—	—	1.20	17.59	1.40	3.05	1.48	—	—	—	—	99.70
Theory	46.97	26.62	—	—	3.48	13.39	4.08	2.70	2.76	—	—	—	—	100.00
CX	46.30	26.20	—	—	3.63	12.88	4.30	2.88	2.80	—	—	—	—	98.99
Theory	47.29	25.66	1.75	—	—	17.16	—	8.14	—	—	—	—	—	100.00
CI	47.67	25.75	2.26	—	—	17.31	—	7.76	—	—	—	—	—	100.75
Theory	46.93	25.48	1.74	—	—	17.03	1.02	7.41	0.39	—	—	—	—	100.00
XXXII	46.82	26.12	1.39	—	0.26	17.23	0.97	6.88	0.33	—	—	—	—	100.00
Theory	45.79	23.79	3.39	—	1.27	21.37	1.00	2.63	0.76	—	—	—	—	100.00
CIV	45.57	23.65	3.38	—	1.23	20.81	0.63	2.46	0.78	—	—	—	—	98.51
Theory	49.40	26.25	2.74	—	0.46	12.81	1.07	4.25	—	—	—	3.02	—	100.00
L	49.49	26.06	2.65	0.25MnO	0.36	12.89	0.80	4.50	—	—	—	3.00	—	100.00
Theory	49.01	27.78	—	—	—	15.25	—	—	—	7.96	—	—	—	100.00
III	49.42	27.50	—	—	—	15.25	—	—	—	7.83	—	—	—	100.00
Theory	49.62	28.12	—	—	—	15.44	1.08	3.56	0.83	1.35	—	—	—	100.00
LXIII	49.30	26.99	—	—	—	15.59	0.69	3.48	0.66	1.35	—	—	—	98.06

K. Scapolites of the type

$$\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 22\,SiO_2$$

			Source	Analyst
58	$14\,MO \cdot 2\,(6\,R_2O_3 \cdot 22\,SiO_2) \cdot 12\,H_2O$	$14\,MO = 7.5\,CaO \cdot 4\,K_2O \cdot 2.5\,MgO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Bolton, Mass.	G. v. Rath
59	$18\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 4\,H_2O$	$18\,MO = 9\,CaO \cdot 7\,Na_2O \cdot 1\,K_2O \cdot 1\,MgO$	St. Lawrence Co., N.S.	„
60	$20\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2)$	$20\,MO = 10\,Na_2O \cdot 9\,CaO \cdot 1\,K_2O$	Monzoni	Kiepen-heuer
61	$20\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 4\,H_2O$	$20\,MO = 7.5\,Na_2O \cdot 7\,CaO \cdot 3.5\,MgO \cdot 1\,K_2O \cdot 1\,H_2O$	Dipyre, Breno	Salomon
62	$14\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 2\,NaCl$	$14\,MO = 10\,CaO \cdot 3\,Na_2O \cdot 1\,K_2O$	Steinhag	Wittstein
63	$14\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 4\,H_2O \cdot 3\,CaCO_3$	$14\,MO = 8.5\,CaO \cdot 0.5\,K_2O \cdot 5\,Na_2O$	French Creek, Pa.	Genth
64	$15\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 2\,H_2O \cdot 2\,NaCl$	$15\,MO = 8.5\,CaO \cdot 6.5\,Na_2O$	Pargas	Rammels-berg
65	$15\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 2\,H_2O \cdot 2\,NaCl$	$15\,MO = 9\,CaO \cdot 4\,Na_2O \cdot 2\,K_2O$	„	„
66	$15\,MO \cdot 2\,(6\,Al_2O_3 \cdot 22\,SiO_2) \cdot 4\,NaCl$	$15\,MO = 9.5\,CaO \cdot 4.5\,Na_2O \cdot 1\,K_2O$	St. Lawrence Co., N.Y.	„

L. Scapolites of the type

$$\bar{Si} \cdot \hat{R} \cdot \bar{Si} \cdot \hat{R} \cdot \bar{Si} \cdot \hat{R} \cdot \bar{Si} = 9\,R_2O_3 \cdot 20\,SiO_2$$

			Source	Analyst
67	$16\,MO \cdot 2\,(9\,Al_2O_3 \cdot 20\,SiO_2) \cdot 18\,H_2O$	$16\,MO = 9\,CaO \cdot 4\,Na_2O \cdot 1.5\,MgO \cdot 1.5\,K_2O$	Saleix, Ariége	Grandeau
68	$24\,MO \cdot 2\,(9\,Al_2O_3 \cdot 20\,SiO_2)$	$24\,MO = 20.5\,CaO \cdot 2.5\,Na_2O \cdot 1\,FeO$	Vesuvius	Gmelin
69	$26\,MO \cdot 2\,(9\,R_2O_3 \cdot 20\,SiO_2) \cdot 6\,H_2O$	$26\,MO = 21\,CaO \cdot 5\,K_2O$ $18\,R_2O_3 = 15\,Al_2O_3 \cdot 3\,Fe_2O_3$	Bolton, Mass.	Muir
70	$22\,MO \cdot 2\,(9\,Al_2O_3 \cdot 20\,SiO_2) \cdot 4\,CaCO_3$	$22\,MO = 19.5\,CaO \cdot 2.5\,Na_2O$	Vesuvius	Gmelin

or the general formulæ

(a) $m\,MO \cdot 2\,(6\,R_2O_3 \cdot 22\,SiO_2) \cdot n\,H_2O$,

(b) $m\,MO \cdot 2\,(6\,R_2O_3 \cdot 22\,SiO_2) \cdot n\,H_2O \cdot p \cdot NaCl$ (or $p \cdot CaCO_3$).

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	52.75	23.42	1.60	—	2.00	8.39	7.51	—	4.33	—	—	—	—	100.00
CVIa	52.20	24.03	1.71	—	1.80	8.06	7.40	0.37	4.43	—	—	—	—	100.00
Theory	52.72	24.44	—	—	0.80	10.06	1.88	8.67	1.43	—	—	—	—	100.00
LXXXIX	52.25	23.97	Trace	—	0.78	9.86	1.73	8.70	1.20	—	—	—	—	98.49
Theory	51.95	24.08	—	—	—	9.92	1.85	12.20	—	—	—	—	—	100.00
VII	52.19	23.54	—	—	—	9.61	2.11	12.65	—	—	—	—	—	100.10
Theory	52.71	24.44	—	—	2.79	7.83	1.88	9.28	1.07	—	—	—	—	100.00
VIII	52.74	23.98	0.40	—	2.77	7.43	1.86	9.00	1.18	—	—	—	—	99.36
Theory	54.76	25.39	—	—	—	11.62	1.95	3.86	—	2.42	—	—	—	100.00
VI	54.87	25.32	—	—	—	11.63	1.50	3.86	—	2.15	—	—	—	99.33
Theory	52.08	24.15	—	—	—	12.70	0.93	6.11	1.42	—	—	2.61	—	100.00
LXXXIV	52.30	23.68	0.58	—	0.05	12.36	0.77	6.29	1.50	—	—	2.63	—	100.16
Theory	54.04	24.91	—	—	—	9.69	—	9.46	0.73	—	—	—	1.48	100.31*
LXI	53.32	24.67	—	—	—	9.84	—	9.12	0.73	—	—	—	1.73	99.41
Theory	53.43	24.60	—	—	—	10.13	3.78	6.23	0.72	—	—	—	1.43	100.32*
LXII	53.32	24.08	—	—	—	9.60	3.93	6.31	0.71	—	—	—	1.71	99.66
Theory	52.93	24.38	—	—	—	10.59	1.87	8.03	—	—	—	—	2.83	101.63*
XCI	52.90	24.95	—	—	—	10.54	1.53	8.10	—	—	—	—	2.33	100.35

or the general formulæ

(a) $m\,MO \cdot 2\,(9\,R_2O_3 \cdot 20\,SiO_2) \cdot n\,H_2O$,

(b) $m\,MO \cdot 2\,(9\,R_2O_3 \cdot 20\,SiO_2) \cdot n\,CaCO_3$.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O	NaCl	$CaCO_3$	CO_2	Cl	Total
Theory	43.54	33.50	—	—	1.09	9.14	2.56	4.49	5.88	—	—	—	—	100.00
XXVII	44.08	32.85	—	—	1.18	9.17	2.68	4.43	6.20	—	—	—	—	100.59
Theory	42.78	32.72	—	1.28	—	20.46	—	2.76	—	—	—	—	—	100.00
X	43.80	32.85	—	1.07	—	20.64	—	2.57	—	—	—	—	—	100.93
Theory	38.94	24.83	7.78	—	—	19.07	7.63	—	1.75	—	—	—	—	100.00
XCVIII	37.81	25.10	7.89	—	—	18.34	7.30	—	1.50	—	—	—	—	97.94
Theory	40.80	31.21	—	—	—	22.37	—	2.63	—	—	—	2.99	—	100.00
IX	40.80	30.60	—	—	—	22.10	—	2.40	—	—	—	3.10	—	100.00

* The excess above 100.00 in the Theory-Total in Nos. 64, 65 and 66 is due to the oxygen-equivalent of the chlorine being included in the figures in the Na_2O column.—A. B. S.

The

The following analyses of the minerals

A. $\overline{Si} \cdot \hat{R} \cdot \overline{Si} = 3\,R_2O_3 \cdot 10\,SiO_2$,

B. $\hat{Si} \cdot \hat{R} \cdot \hat{Si} = 3\,R_2O_3 \cdot 12\,SiO_2$,

C. $\hat{R}\begin{cases}\overline{Si}\\ \overline{Si}\\ \overline{Si}\end{cases} = 3\,R_2O_3 \cdot 15\,SiO_2$,

D. $\hat{R}\begin{cases}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{cases} = 3\,R_2O_3 \cdot 18\,SiO_2$,

E. $\overline{R} \cdot \hat{Si} \cdot \overline{R} = 5\,R_2O_3 \cdot 6\,SiO_2$,

F. $\hat{Si} \cdot \overline{R} \cdot \overline{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 12\,SiO_2$,

A. Orthochlorites of the type

$\overline{Si} \cdot \hat{R} \cdot \overline{Si} = 3\,R_2O_3 \cdot 10\,SiO_2$

				Source
1	$22\,MO \cdot 2\,(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 16\,H_2O$	$22\,MO = 12.5\,FeO \cdot 7\,MgO \cdot 1\,CaO \cdot 0.5\,MnO \cdot 0.5\,K_2O \cdot 0.5\,Na_2O$	Ortho-chlorite	Bishops Hill
2	$31\,MO \cdot 2\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot 26\,H_2O$	$31\,MO = 27\,MgO \cdot 3.5\,FeO \cdot 0.5\,CaO$; $6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,Fe_2O_3$	Delessite	St. Cyrus, Scotland
3	$32\,MO\ \ 2\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot 24\,H_2O$	$32\,MO = 30\,MgO \cdot 2\,FeO$; $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Orthochlorite (Clinochlorite)	Kupferberg
4	$34\,MO \cdot 2\,(3\,Al_2O_3 \cdot 10\,SiO_2) \cdot 26\,H_2O$	$34\,MO = 31\,MgO \cdot 3\,FeO$	Orthochlorite	Zillertal
5	$43\,MO \cdot 2\,(3\,R_2O_3 \cdot 10\,SiO_2) \cdot 8\,H_2O$	$43\,MO = 40.5\,MgO \cdot 2.5\,FeO$; $6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,Cr_2O_3$	„	Webster, N.C.

B. Orthochlorites of the types

$\hat{Si} \cdot \hat{R} \cdot \hat{Si} = 3\,R_2O_3 \cdot 12\,SiO_2$

				Source
6	$25\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 22\,H_2O$	$25\,MO = 25\,MgO$ $6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,Fe_2O_3$	Lennilite	Petham, Mass.
7	$33\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 28\,H_2O$	$33\,MO = 19MgO \cdot 6FeO \cdot 7CaO \cdot 1K_2O$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Orthochlorite (Pennine)	Corry-charmaig
8	$33\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 28\,H_2O$	$33\,MO = 31\,MgO \cdot 1\,FeO \cdot 1\,CaO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Cr_2O_3$	Orthochlorito	Bissersk
9	$36\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 24\,H_2O$	$36\,MO = 31.5\,MgO \cdot 1.5\,FeO \cdot 1.5\,K_2O \cdot 1\,Na_2O \cdot 0.5\,Li_2O$	„	Tilly Foster Mine, N.Y.
10	$38\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 28\,H_2O$	$38\,MO = 37\,MgO \cdot 1\,FeO$ $6\,R_2O_3 = 4.5\,Al_2O_3 \cdot 1.5\,Cr_2O_3$	„	Itkul Sea
11	$38\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 38\,H_2O$	$38\,MO = 38\,MgO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	Calumet Falls, Can.
12	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$39\,MO = 39\,MgO$ $6\,R_2O_3 = 4.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3 \cdot 1\,Cr_2O_3$	„	Texas, Pa.

Orthochlorite Group

of the orthochlorite group conform to the following types :

G. $\hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} = 5\,\mathrm{R_2O_3} \cdot 18\,\mathrm{SiO_2}$,
H. $\overline{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} \cdot \overline{\mathrm{Si}} = 5\,\mathrm{R_2O_3} \cdot 22\,\mathrm{SiO_2}$,
J. $\hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} = 6\,\mathrm{R_2O_3} \cdot 6\,\mathrm{SiO_2}$,
K. $\overline{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{R}} \cdot \overline{\mathrm{Si}} = 6\,\mathrm{R_2O_3} \cdot 10\,\mathrm{SiO_2}$,
L. $\hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} = 6\,\mathrm{R_2O_3} \cdot 12\,\mathrm{SiO_2}$,
M. $\overline{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \overline{\mathrm{Si}} = 6\,\mathrm{R_2O_3} \cdot 16\,\mathrm{SiO_2}$,
N. $\hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} = 6\,\mathrm{R_2O_3} \cdot 18\,\mathrm{SiO_2}$,
O. $\overline{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \overline{\mathrm{R}} = 8\,\mathrm{R_2O_3} \cdot 12\,\mathrm{SiO_2}$,
P. $\hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} \cdot \hat{\mathrm{Si}} \cdot \hat{\mathrm{R}} = 9\,\mathrm{R_2O_3} \cdot 12\,\mathrm{SiO_2}$.

or the general formula

$\mathrm{m\,MO} \cdot 2\,(3\,\mathrm{R_2O_3} \cdot 10\,\mathrm{SiO_2}) \cdot \mathrm{n\,H_2O}$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Heddle	Theory	34.89	17.79	—	—	26.16	1.03	1.34	8.14	1.37	0.90	8.38	100.00
	LXIX	35.41	18.08	0.48	—	26.47	0.61	1.01	8.77	0.98	0.52	8.03	100.36
,,	Theory	32.45	13.79	4.33	—	6.81	—	0.76	29.20	—	—	12.66	100.00
	V	32.69	13.44	4.40	—	6.62	—	0.86	28.77	—	—	13.25	100.03
Kobell	Theory	33.17	15.51	2.23	—	3.98	—	—	33.17	—	—	11.94	100.00
	III	33.49	15.37	2.30	0.55	4.25	—	—	32.94	—	—	11.50	100.40
Brüel	Theory	32.12	16.38	—	—	5.78	—	—	33.19	—	—	12.53	100.00
	XXIII	31.47	16.67	—	—	5.97	0.11	—	32.56	—	—	12.43	99.21
Genth	Theory	31.53	13.40	—	3.99	4.74	—	—	42.56	—	—	3.78	100.00
	CLX	31.45	13.08	—	4.16	4.88	—	0.17	43.10	0.06	0.16 NiO	3.29	100.35

or the general formula

$\mathrm{m\,MO} \cdot 2\,(3\,\mathrm{R_2O_3} \cdot 12\,\mathrm{SiO_2}) \cdot \mathrm{n\,H_2O}$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Gooch	Theory	41.07	14.55	4.56	—	—	—	—	28.53	—	—	11.09	100.00
	III	41.27	15.19	4.14	—	—	—	—	28.25	—	—	11.32	100.17
Heddle	Theory	33.78	13.16	1.88	—	10.13	—	9.19	17.83	2.20	—	11.83	100.00
	LXII	34.31	13.64	0.36	—	10.31	0.23	8.97	18.14	1.36	0.13	12.41	99.76
Hartwall	Theory	36.83	14.36	—	1.94	1.84	—	1.43	30.69	—	—	12.91	100.00
	CXI	37.00	14.20	—	1.00	1.50	—	1.50	31.50	—	—	13.00	99.70
Schlaepfer	Theory	35.38	15.04	—	—	2.65	—	0.38 Li_2O	30.95	3.46	1.52	10.62	100.00
	CXXVII	36.18	14.34	0.28	—	2.88	—	0.42 Li_2O	31.26	3.09	1.99	10.31	100.75
Hermann	Theory	34.42	10.97	—	5.46	1.72	—	—	35.38	—	—	12,05	100.00
	CXIII	34.64	10.50	—	5.50	2.00	—	—	35.47	—	—	12.03	100.14
Hunt	Theory	33.61	13.09	1.87	—	—	—	—	35.47	—	—	15.96	100.00
	CXVIII	33.28	13.30	1.92	—	—	—	—	35.50	—	—	16.00	100.00
Smith und Brush	Theory	34.03	10.84	1.89	3.60	—	—	—	36.87	—	—	12.77	100.00
	CXLIV	33.26	10.69	1.96	4.78	—	—	—	35.93	—	0.35	12.64	99.61

				Source
13	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$39\,MO = 39\,MgO$ $6\,R_2O_3 = 4.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3 \cdot 1Cr_2O_3$	Orthochlorite	Texas, Pa.
14	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$39\,MO = 37\,MgO \cdot 2\,FeO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	Zillertal
15	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$39\,MO = 37\,MgO \cdot 2\,FeO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	„
16	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$39\,MO = 37\,MgO \cdot 2\,FeO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	Naßfeld
17	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$39\,MO = 37\,MgO \cdot 2\,FeO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	Zermatt
18	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$39\,MO = 37\,MgO \cdot 2\,FeO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	„
19	$39\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$39\,MO = 37\,MgO \cdot 2\,FeO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	„
20	$40\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$40\,MO = 37\,MgO \cdot 3\,FeO$	„	Binnenthal
21	$40\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	„ „ „	„	Zermatt
22	$40\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	„ „ „	„	„
23	$40\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	„ „ „	„	„
24	$40\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$40\,MO = 38.5\,MgO \cdot 1.5\,MnO$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	„	Pojsberg
25	$43\,MO \cdot 2\,(3\,Al_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$43\,MO = 25.5\,MgO \cdot 17.5\,FeO$	Diabantite	Landesfreude
26	$45\,MO \cdot 2\,(3\,R_2O_3 \cdot 12\,SiO_2) \cdot 30H_2O$	$45\,MO = 36MgO \cdot 7FeO \cdot 1\,MnO \cdot 1Na_2O$ $6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,Fe_2O_3$	Orthochlorite	Sealpay

C. Orthochlorites of the type

$$\hat{R}\left\langle\begin{matrix}\bar{Si}\\ \bar{Si}\\ \bar{Si}\end{matrix}\right. = 3\,R_2O_3 \cdot 15\,SiO_2$$

				Source
27	$32\,MO \cdot 2\,(3\,Al_2O_3 \cdot 15\,SiO_2) \cdot 42\,H_2O$	$32\,MO = 29MgO \cdot 3\,FeO$	Orthochlorite	North Burgess, Can.
28	$32\,MO \cdot 2\,(3\,R_2O_3 \cdot 15\,SiO_2) \cdot 54\,H_2O$	$32\,MO = 32\,MgO$ $6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,Fe_2O_3$	„	Culsagee Mine, N.C.
29	„ „ „ „	$32\,MO = 32\,MgO$ $6\,R_2O_3 = 5\,Al_2O_3 \cdot 1\,Fe_2O_3$	„	„
30	$39\,MO \cdot 2\,(3\,Al_2O_3 \cdot 15\,SiO_2) \cdot 20\,H_2O$	$39\,MO = 32\,MgO \cdot 7\,FeO$	„	Traversella
31	$48\,MO \cdot 2\,(3\,Al_2O_3 \cdot 15\,SiO_2) \cdot 38\,H_2O$	$48\,MO = 44\,MgO$ $\cdot 2\,FeO \cdot 1\,CaO \cdot 1\,MnO$	„	Beautyhill
32	$53\,MO \cdot 2\,(3\,Al_2O_3 \cdot 15\,SiO_2) \cdot 36\,H_2O$	$53\,MO = 47\,MgO \cdot 6\,FeO$	„	Zermatt
33	„ „ „ „	„ „ „	„	„

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Smith and Brush	Theory	34.03	10.84	1.89	3.60	—	—	—	36.87	—	—	12.77	100.00
	CXLV	33.30	10.50	1.60	4.67	—	—	—	36.08	0.35 Alk	—	13.25	99.75
Rumpf	Theory	33.60	13.10	1.83	—	3.36	—	—	34.57	—	—	13.48	100.00
	XXIV	34.24	12.64	1.64	—	3.35	—	0.30	34.86	—	—	14.44	101.15
Ludwig	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XXV	33.83	12.95	2.25	—	3.02	—	—	34.94	—	—	13.11	100.10
Telek	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XXI	33.44	13.72	3.40	—	3.26	—	—	32.99	—	—	12.71	99.52
Schlaepfer	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XLVII	34.06	11.75	1.92	0.69	2.78	—	—	33.90	0.39	2.45	13.08	101.02
v. Fellenberg	Theory	—	—	—	—	—	—	—	—	—	—		—
	XLIV	33.12	13.25	1.52	0.60	4.69	—	—	34.04	—	—	12.87	100.09
v. Hamm	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XLVI	33.71	12.55	2.74	—	3.40	—	0.66	34.70	—	—	12.27	100.03
Marignac	Theory	33.58	14.27	—	—	5.04	—	—	34.52	—	—	12.59	100.00
	XLVIII	33.95	13.46	—	0.24	6.12	—	—	33.71	—	—	12.52	100.00
„	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XXXVIII	33.36	13.24	—	0.20	5.93	—	—	34.21	—	—	12.80	99.74
„	Theory	33.58	14.27	—	—	5.04	—	—	34.52	—	—	12.59	100.00
	XXXIX	33.40	13.41	—	0.15	5.73	—	—	34.57	—	—	12.74	100.00
Wartha	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XLIII	32.51	14.55	—	—	4.96	—	—	34.01	—	—	14.07	100.10
Hamberg	Theory	33.73	13.14	1.87	—	2.53	—	—	36.08	—	—	12.65	100.00
	LXXXVIII	33.71	13.80	1.64	—	2.28	—	—	35.88	—	—	13.11	100.75
Liebe	Theory	29.56	12.57	—	—	25.86	—	—	20.94	—	—	11.08	100.00
	II	29.37	12.00	—	—	25.63	—	0.33	21.01	—	—	11.27	99.28
Heddle	Theory	30.40	10.77	3.38	—	10.60	1.50	—	30.40	—	1.52	11.43	100.00
	LXI	30.41	11.58	2.34	—	10.71	1.19	—	30.63	0.01	1.31	11.74	99.92

or the general formula

$$m\,MO \cdot 2\,(3\,R_2O_3 \cdot 15\,SiO_2) \cdot n\,H_2O.$$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Hunt	Theory	39.61	13.47	—	—	4.75	25.53	—	—	—	—	16.64	100.00
	CXX	39.30	14.25	—	—	4.41	25.73	—	—	—	—	16.93	100.62
Chatard	Theory	38.12	10.80	3.38	—	—	—	—	27.12	—	—	20.58	100.00
	CLVIII	38.29	11.41	1.95	—	0.32	0.25(Ni,Co)O	—	26.40	—	—	21.25	99.87
Clarke & Schneider	Theory	38.12	10.80	3.38	—	—	—	—	27.12	—	—	20.58	100.00
	CLIX	38.13	11.22	2.28	—	0.18	0.48 NiO	—	27.39	—	—	20.47	100.15
Marignac	Theory	39.51	13.44	—	—	11.06	—	—	28.09	—	—	7.90	100.00
	LIV	39.81	12.56	—	—	11.10	—	—	28.41	—	—	7.79	99.67
Heddle	Theory	35.11	11.94	—	—	2.81	1.38	1.09	34.33	—	—	13.34	100.00
	LXV	34.73	12.44	—	—	2.68	1.17	1.60	34.10	—	—	13.10	99.82
Max Donnell	Theory	33.51	11.39	—	—	8.01	—	—	35.00	—	—	12.09	100.00
	XL	33.64	10.64	—	—	8.83	—	—	34.95	—	—	12.40	100.46
Merz	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	XLI	33.26	11.69	—	—	7.20	—	—	35.18	—	—	12.18	99.51

D. Orthochlorites of the type

$$\hat{R} \left\langle \begin{matrix} \hat{Si} \\ \hat{Si} \\ \hat{Si} \end{matrix} \right. = 3\,R_2O_3 \cdot 18\,SiO_2$$

				Source
34	$46\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 22\,H_2O$	$46\,MO = 39\,MgO \cdot 7\,FeO$	Orthochlorite	Traversella
35	$48\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 24\,H_2O$	$48MO = 35MgO \cdot 6FeO \cdot 3CaO \cdot 3\,Na_2O \cdot 1\,K_2O$	”	Hillswick
36	$50\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 26\,H_2O$	$50\,MO = 40\,MgO \cdot 10\,FeO$	”	Traversella
37	$50\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 46\,H_2O$	$50\,MO = 42\,MgO \cdot 8\,FeO$	”	North Elmsley, Can.
38	$59\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 64\,H_2O$	$59\,MO = 32.5\,MgO \cdot 26.5FeO$	Diabantite	Hölletal
39	$63\,MO \cdot 2\,(3\,Al_2O_3 \cdot 18\,SiO_2) \cdot 44\,H_2O$	$63\,MO = 53\,MgO \cdot 10\,FeO$	Orthochlorite	Zermatt
40	” ” ” ”	” ” ”	”	”

E. Orthochlorites of the type

$$\bar{R} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 6\,SiO_2$$

				Source
41	$24\,MO \cdot 2\,(5\,Al_2O_3 \cdot 6\,SiO_2 \cdot 20\,H_2O$	$24\,MO = 16.5\,MgO \cdot 7.5\,FeO$	Orthochlorite	Chester, Mass.

F. Orthochlorites of the type

$$\hat{Si} \cdot \bar{R} \cdot \bar{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 12\,SiO_2$$

				Source
42	$12\,MO \cdot 2(5\,R_2O_3 \cdot 12\,SiO_2) \cdot 28\,H_2O$	$12\,MO = 8MgO \cdot 2.5CaO \cdot 1MnO \cdot 0.5K_2O \cdot 10\,R_2O_3 = 6.5\,Al_2O_3 \cdot 3.5\,Fe_2O_3$	Hullite	Kinkell
43	$22\,MO \cdot 2(5\,Al_2O_3 \cdot 12SiO_2) \cdot 24\,H_2O$	$22\,MO = 21\,MgO \cdot 0.5\,CaO \cdot 0.5\,FeO$	Orthochlorite	Markirch
44	$29\,MO \cdot 2(5\,R_2O_3 \cdot 12\,SiO_2) \cdot 38\,H_2O$	$29\,MO = 29\,FeO$ $10\,R_2O_3 = 9\,Al_2O_3 \cdot 1\,Fe_2O_3$	Chamosite	Schmiedefeld
45	$33\,MO \cdot 2(5\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$33\,MO = 17.5\,MgO \cdot 11\,FeO \cdot 4.5\,CaO$ $10\,R_2O_3 = 7\,Al_2O_3 \cdot 3\,Fe_2O_3$	Chloropite	Chloropitschiefer von Köditz
46	$34\,MO \cdot 2(5\,R_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$34\,MO = 20.5\,MgO \cdot 12.5\,FeO \cdot 1\,CaO$ $10\,R_2O_3 = 8{,}5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	Delessite	Friedrichsroda
47	$36\,MO \cdot 2(5\,Al_2O_3 \cdot 12SiO_2) \cdot 36\,H_2O$	$36\,MO = 33\,FeO \cdot 3\,MgO$	Chamosite	Chrustenic
48	$38\,MO \cdot 2(5\,Al_2O_3 \cdot 12SiO_2) \cdot 32\,H_2O$	$38\,MO = 35\,MgO \cdot 3\,FeO$	Orthochlorite	Newlin, Pa.
49	$40\,MO \cdot 2(5\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$40\,MO = 40\,MgO$ $10\,R_2O_3 = 8.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	”	Alatal
50	$40\,MO \cdot 2(5\,R_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$40\,MO = 40\,MgO$ $10\,R_2O = 8.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	”	Achmatowsk

or the general formula

$m\,MO \cdot 2\,(3\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O.$

Analyst.		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Marignac	Theory	41.28	11.70	—	—	9.63	—	—	29.82	—	—	7.57	100.00
	LV	41.34	11.42	—	—	10.09	—	—	29.67	—	—	7.66	100.18
Heddle	Theory	39.39	11.16	—	—	7.88	—	3.06	25.53	1.71	3.39	7.88	100.00
	LXXVIII	39.81	11.43	—	—	7.97	0.26	2.80	25.65	1.20	3.15	7.91	100.18
Marignac	Theory	38.84	11.01	—	—	12.94	—	—	28.76	—	—	8.45	100.00
	LIII	38.45	11.75	—	—	12.82	—	—	28.19	—	—	8.49	99.70
Hunt	Theory	36.88	10.45	—	—	9.84	—	—	28.69	—	—	14.14	100.00
	CXIX	36.70	10.96	—	—	9.36	—	—	28.19	—	—	14.31	99.52
Liebe	Theory	30.29	8.58	—	—	26.75	—	—	18.23	—	—	16.15	100.00
	V	29.85	9.07	—	—	26.60	—	—	17.92	—	—	15.81	99.25
Schweizer	Theory	33.73	9.56	—	—	11.24	—	—	33.10	—	—	12.37	100.00
	XXXVI	33.82	9.32	—	—	11.30	—	—	33.04	—	—	11.50	98.98
”	Theory												
	XXXVII	33.07	9.69	—	—	11.36	—	—	32.34	—	—	12.58	99.04

or the general formula

$m\,MO \cdot 5\,(5\,R_2O_3 \cdot 6\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Pisani	Theory	21.81	30.91	—	—	16.36	—	—	20.00	—	—	10.91	100.00
	CXXIV	21.40	32.30	—	—	15.80	—	—	19.90	—	—	10.90	100.30

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Heddle	Theory	38.45	17.71	14.95	—	—	1.90	3.74	8.54	1.25	—	13.46	100.00
	II	38.59	17.34	15.97	—	—	1.56	3.94	8.65	0.67	—	13.48	100.20
Delesse	Theory	37.94	26.87	—	—	0.94	—	0.74	22.13	—	—	11.38	100.00
	I	38.39	26.54	—	—	0.59	—	0.67	22.16	—	—	11.65	100.00
Loretz	Theory	27.22	17.35	3.02	—	39.47	—	—	—	—	—	12.94	100.00
	III	27.00	17.00	4.00	—	39.00	—	—	—	—	—	13.00	100.00
”	Theory	29.07	14.41	9.69	—	15.99	—	5.08	14.13	—	—	11.63	100.00
	IV	29.06	14.04	9.27	—	15.96	—	5.02	13.95	—	—	11.64	98.94
Pufahl	Theory	29.18	17.57	4.86	—	18.24	—	1.13	16.61	—	—	12.41	100.00
	IV	28.79	16.74	4.83	—	18.30	—	0.98	16.62	—	—	12.25	100.21
Bořicky	Theory	25.69	18.20	—	—	42.40	—	—	2.14	—	—	11.57	100.00
	VI	25.60	18.72	—	—	42.31	—	—	2.13	—	—	11.24	100.00
Leeds	Theory	30.96	21.92	—	—	4.64	—	—	30.09	—	—	12.39	100.00
	CXXXVII	30.62	21.73	0.42	—	5.01	—	—	29.69	0.11 Li_2O	0.14	12.26	99.98
Marignac	Theory	30.49	18.36	5.08	—	—	—	—	33.88	—	—	12.19	100.00
	L	30.01	19.11	4.81	—	—	—	—	33.15	—	—	12.52	99.60
”	Theory	30.49	18.36	5.08	—	—	—	—	33.88	—	—	12.19	100.00
	XCI	30.27	19.85	4.42	—	—	—	—	33.13	—	—	12.54	100.25

				Source
51	$40\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 32\ H_2O$	$40\ MO = 23.5\ MgO \cdot 16.5\ FeO$	Orthochlorite	Gumuch, Dagh.
52	$40\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 34\ H_2O$	$40\ MO = 22\ MgO \cdot 18\ FeO$	,,	Sept-Lacs
53	$40\ MO \cdot 2(5\ R_2O_3 \cdot 12\ SiO_2) \cdot 34\ H_2O$	$40\ MO = 38\ MgO \cdot 2\ FeO$ $10\ R_2O_3 = 9\ Al_2O_3 \cdot 1\ Fe_2O_3$	,,	Borostyankö
54	$40\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 40\ H_2O$	$40\ MO = 38\ MgO \cdot 2\ FeO$	,,	Alatal
55	$40\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 40\ H_2O$	,, ,, ,,	,,	,,
56	$41\ MO \cdot 2(5\ R_2O_3 \cdot 12\ SiO_2) \cdot 34\ H_2O$	$41\ MO = 37\ MgO \cdot 4\ FeO$ $10\ R_2O_3 = 9.5\ Al_2O_3 \cdot 0.5\ Fe_2O_3$	,,	Montafun
57	$41\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 46\ H_2O$	$41\ MO = 34\ FeO \cdot 5\ MgO \cdot 1\ CaO \cdot 1\ K_2O$	Metachlorite	Büchenberge bei Elbingerode
58	$42\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 32\ H_2O$	$42\ MO = 38\ MgO \cdot 4\ FeO$	Orthochlorite	Culsagee Mine, N.C.
59	$42\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 34\ H_2O$	$42\ MO = 41.5\ MgO \cdot 0.5\ FeO$	,,	Amity, N.Y.
60	$42\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 46\ H_2O$	$42\ MO = 21\ MgO \cdot 20\ FeO \cdot 1\ Na_2O$	,,	Foundry Run, Georget, D.C.
61	$46\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 28\ H_2O$	$46\ MO = 24\ MgO \cdot 22\ FeO$	,,	St. Gotthard
62	$46\ MO \cdot 2(5\ Al_2O_3 \cdot 12\ SiO_2) \cdot 38\ H_2O$	$46\ MO = 33\ MgO \cdot 12\ FeO \cdot 1\ CaO$	,,	Zillertal
63	$47\ MO \cdot 2(5\ R_2O_3 \cdot 12\ SiO_2) \cdot 36\ H_2O$	$47\ MO = 33.5 MgO \cdot 12.5 FeO \cdot 1 MnO$ $10\ R_2O_3 = 9.5\ Al_2O_3 \cdot 0.5\ Fe_2O_3$	,,	Loch Laggan

G. Orthochlorites of the type

$$\hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si} = 5\ R_2O_3 \cdot 18\ SiO_2$$

				Source
64	$42\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 36\ H_2O$	$42\ MO = 42\ MgO$ $10\ R_2O_3 = 7.5\ Al_2O_3 \cdot 2.5\ Fe_2O_3$	Lennilite	Lenni
65	$44\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 34\ H_2O$	$44\ MO = 37.5\ MgO \cdot 3.5\ FeO \cdot 3\ CaO$ $10\ R_2O_3 = 7.5\ Al_2O_3 \cdot 2.5\ Fe_2O_3$	Berlauite	Berlaubach bei Budweis
66	$44\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 40\ H_2O$	$44\ MO = 28.5\ MgO \cdot 14\ FeO \cdot 1.5\ CaO$ $10\ R_2O_3 = 7.5\ Al_2O_3 \cdot 2.5\ Fe_2O_3$	Euralite	Kiperjärvi
67	$44\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_3) \cdot 58\ H_2O$	$44\ MO = 37.5\ MgO \cdot 3.5\ FeO \cdot 3\ CaO$ $10\ R_2O_3 = 7.5\ Al_2O_3 \cdot 2.5\ Fe_2O_3$	Berlauite	Berlaubach bei Budweis
68	$53\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$53\ MO = 53\ MgO$ $10\ R_2O_3 = 7\ Al_2O_3 \cdot 3\ Fe_2O_3$	Ortho-chlorite	Snarum
69	$54\ MO \cdot 2(5\ Al_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$54\ MO = 53\ MgO \cdot 1\ FeO$	,,	Ploben
70	$56\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 54\ H_2O$	$56\ MO = 33\ MgO \cdot 18\ FeO \cdot 2\ CaO \cdot 1\ MnO \cdot 1.5 Na_2O \cdot 0.5 K_2O; 10 R_2O_3 = 9 Al_2O_3 \cdot 1 Fe_2O_3$	Delessite	Elie, Fifeshire
71	$57\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$57\ MO = 57\ MgO$ $10\ R_2O_3 = 7\ Al_2O_3 \cdot 2.5\ Cr_2O_3 \cdot 0.5\ Fe_2O_3$	Ortho-chlorite	Texas, Pa.
72	$57\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$57\ MO = 57\ MgO$ $10\ R_2O_3 = 7\ Al_2O_3 \cdot 2.5\ Cr_2O_3 \cdot 0.5\ Fe_2O_3$	,,	,, ,,

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
L. Smith	Theory	27.88	19.75	—	—	23.01	—	—	18.21	—	—	11.15	100.00
	CXIV	27.20	18.62	—	—	23.21	—	—	17.64	—	—	10.61	97.28
Marignac	Theory	27.44	19.44	—	—	24.70	—	—	16.77	—	—	11.65	100.00
	LX	27.14	19.19	—	—	24.76	—	—	16.78	—	—	11.50	99.37
Szilasi	Theory	30.04	19.15	3.34	—	3.00	—	—	31.71	—	—	12.76	100.00
	XVI	30.45	18.96	3.70	—	2.21	—	—	32.20	—	—	12.79	100.31
Jannasch	Theory	29.73	21.06	—	—	2.97	—	—	31.37	—	—	14.87	100.00
	LI	29.31	21.31	0.07	—	3.24	—	—	31.28	—	0.43	14.58	100.22
„	Theory	—	—	—	—	—	—	—	—	—	—	—	—
	LII	29.59	24.82(Al_2O_3+FeO)			—	—	—	31.46	—	0.30	14.73	100.90
Wartha	Theory	29.57	19.91	1.64	—	5.91	—	—	30.41	—	—	12.56	100.00
	XXXII	29.44	20.98	2.00	—	5.60	—	—	30.31	—	—	12.29	100.62
List	Theory	23.65	16.76	—	—	40.22	—	0.93	3.28	1.55	—	13.61	100.00
	I	23.78	16.43	—	—	40.37	—	0.74	3.10	1.38	0.08	13.76	99.64
Genth	Theory	29.73	21.06	—	—	5.94	—	—	31.38	—	—	11.89	100.00
	CLVI	29.48	22.22	0.70	—	5.30	0.17	—	30.99	0.11(NiCo)O		11.63	100.60
Sipöcz	Theory	30.20	21.40	—	—	0.76	—	—	34.81	—	—	12.83	100.00
	CXXV	30.28	22.13	—	—	1.08	—	—	34.45	—	—	12.61	100.55
Clarke	Theory	25.57	18.11	—	—	25.57	—	—	14.92	—	1.09	14.70	100.00
	CLI	25.45	17.88	—	—	24.98	—	—	15.04	—	0.67	14.43	98.45
Varren-trapp	Theory	26.14	18.52	—	—	28.76	—	—	17.43	—	—	9.15	100.00
	XXXIII	25.37	18.50	—	—	28.79	—	—	17.09	—	—	8.96	98.71
Tscher-mak	Theory	26.69	18.91	—	—	16.02	—	1.04	24.47	—	—	12.87	100.00
	XXXI	26.30	19.80	—	—	15.10	—	1.00	24.40	—	—	12.40	99.00
Heddle	Theory	26.42	17.79	1.47	—	16.52	1.30	—	24.59	—	—	11.91	100.00
	LXXV	26.25	19.22	1.67	—	16.44	1.02	—	24.35	—	—	11.67	100.62

or the general formula

$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Gooch	Theory	38.21	13.53	7.08	—	—	—	—	29.72	—	—	11.46	100.00
	II	38.03	12.93	7.02	—	0.50	—	—	29.64	—	—	11.68	99.80
Schrauf	Theory	36.88	13.05	6.83	—	4.31	—	2.86	25.62	—	—	10.45	100.00
	II	37.25	13.75	6.86	—	4.02	—	2.81	25.77	—	—	9.82	100.28
Wilk	Theory	34.41	12.18	6.37	—	16.06	—	1.34	18.16	—	—	11.48	100.00
	I	33.68	12.15	6.80	—	15.66	—	1.34	17.92	—	—	11.49	99.04
Schrauf	Theory	34.35	12.16	6.36	—	4.00	—	2.67	23.85	—	—	16.61	100.00
	I	34.38	12.69	6.33	—	3.71	—	2.59	23.79	—	—	16.79	100.28
Rammels-berg	Theory	34.07	11.27	7.57	—	—	—	—	33.45	—	—	13.64	100.00
	LXXIX	34.88	12.48	5.81	—	—	—	—	34.02	—	—	13.68	100.87
v. Drasche	Theory	34.64	16.35	—	—	1.14	—	—	34.00	—	—	13.87	100.00
	XII	34.63	17.13	—	—	1.61	—	—	33.38	—	—	13.93	100.68
Heddle	Theory	30.22	12.84	2.24	—	18.14	0.99	1.56	18.46	0.65	1.30	13.60	100.00
	IX	30.69	12.83	1.63	—	18.32	1.00	1.59	18.60	0.57	1.11	13.77	100.11
Genth	Theory	33.34	11.02	1.24	5.88	—	—	—	35.19	—	—	13.33	100.00
	CXLII	33.20	11.11	1.43	6.85	—	—	—	35.54	0.38 Alk	—	12.95	101.46
Dieffen-bach	Theory	33.34	11.02	1.24	5.88	—	—	—	35.19	—	—	13.33	100.00
	CXLVI	33.04	11.09	1.33	5.91	—	—	—	34.30	0.38 Alk	—	12.81	98.86

				Source
73	$58\ MO \cdot 2(5\ Al_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$58\ MO = 56\ MgO \cdot 2\ FeO$	Ortho-chlorite	Zdjar-Berg
74	$60\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$60\ MO = 54\ MgO \cdot 5\ FeO \cdot 1\ CaO$ $10\ R_2O_3 = 9\ Al_2O_3 \cdot 1\ Fe_2O_3$	„	Hillswick
75	$61\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$61\ MO = 60\ MgO \cdot 1\ FeO$ $10\ R_2O_3 = 5\ Al_2O_3 \cdot 5\ Cr_2O_3$	„ „	Green Valley Cal.
76	$61\ MO \cdot 2(5\ Al_2O_3 \cdot 18\ SiO_2) \cdot 44\ H_2O$	$61\ MO = 55\ MgO \cdot 6\ FeO$	„	Zillertal
77	$63\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 52\ H_2O$	$63\ MO = 60\ MgO \cdot 2\ FeO \cdot 1\ CaO$ $10\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Cr_2O_3$	„ „	Texas, Pa.
78	$63\ MO \cdot 2(5\ R_2O_3 \cdot 18\ SiO_2) \cdot 52\ H_2O$	$63\ MO = 60\ MgO \cdot 2\ FeO \cdot 1\ CaO$ $10\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Cr_2O_3$	„	„ „
79	$65\ MO \cdot 2(5\ Al_2O_3 \cdot 18\ SiO_2) \cdot 44\ H_2O$	$65\ MO = 58\ MgO \cdot 5\ FeO \cdot 1\ CaO \cdot 0.5\ K_2O \cdot 0.5\ Na_2O$	„	Tilly Foster Mine, N.Y.

H. Orthochlorites of the type

$$\bar{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \bar{Si} = 5\ R_2O_3 \cdot 22\ SiO_2$$

				Source
80	$42\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 36\ H_2O$	$42\ MO = 33\ MgO \cdot 8\ FeO \cdot 1\ CaO$ $10\ R_2O_3 = 6.5\ Al_2O_3 \cdot 3.5\ Fe_2O_3$	Epichlorite	Harz
81	$46\ MO \cdot 2(5\ Fe_2O_3 \cdot 22\ SiO_2) \cdot 50\ H_2O$	$46\ MO = 46\ FeO$	Cron-stedtite	Přibram
82	$51\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 48\ H_2O$	$51\ MO = 48.5\ MgO \cdot 2.5\ FeO$ $10\ R_2O_3 = 9\ Al_2O_3 \cdot 1\ Fe_2O_3$	Lennilite	Křemže
83	$52\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 52\ H_2O$	$52MO = 44MgO \cdot 5CaO \cdot 2.5FeO \cdot 0.5\ NiO$ $10\ R_2O_3 = 8\ Al_2O_3 \cdot 2\ Cr_2O_3$	Ortho-chlorite	Texas, Pa.
84	$60\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 24\ H_2O$	$60\ MO = 51\ MgO \cdot 3\ K_2O \cdot 3\ FeO \cdot 3\ Na_2O$ $10\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	„	Taberg
85	$60\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 44\ H_2O$	$60\ MO = 32\ MgO \cdot 27\ FeO \cdot 1\ CaO$ $10\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	Diabantite	Farmington Hills
86	$60\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 44\ H_2O$	$60\ MO = 32\ MgO \cdot 27\ FeO \cdot 1\ CaO$ $10\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	„	„
87	$69\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 52\ H_2O$	$69\ MO = 41.5\ MgO \cdot 27.5\ FeO$ $10\ R_2O_3 = 8\ Al_2O_3 \cdot 2\ Fe_2O_3$	„	Trillochtal
88	$72\ MO \cdot 2(5\ Al_2O_3 \cdot 22\ SiO_2) \cdot 56\ H_2O$	$72\ MO = 47\ MgO \cdot 25\ FeO$	„	Landes-freude
89	$72\ MO \cdot 2(5\ Al_2O_3 \cdot 22\ SiO_2) \cdot 56\ H_2O$	„ „ „	„	„
90	$72\ MO \cdot 2(5\ Al_2O_3 \cdot 22\ SiO_2) \cdot 56\ H_2O$	„ „ „	„	Gräfenwart
91	$73\ MO \cdot 2(5\ Al_2O_3 \cdot 22\ SiO_2) \cdot 54\ H_2O$	$73\ MO = 66\ MgO \cdot 7\ FeO$	Ortho-chlorite	Zermatt
92	$74\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_2) \cdot 64\ H_2O$	$74\ MO = 66\ MgO \cdot 6\ CaO \cdot 2\ FeO$ $10\ R_2O_3 = 6\ Al_2O_3 \cdot 4\ Cr_2O_3$	„	Unst
93	$75\ MO \cdot 2(5\ R_2O_3 \cdot 22\ SiO_3) \cdot 58\ H_2O$	$75\ MO = 73\ MgO \cdot 2\ FeO$ $10\ R_2O_3 = 9\ Al_2O_3 \cdot 1\ Fe_2O_3$	„	Zermatt
94	$79\ MO \cdot 2(5\ Al_2O_3 \cdot 22\ SiO_2) \cdot 50\ H_2O$	$79\ MO = 46.5\ MgO \cdot 32.5\ FeO$	Diabantite	Reinsdorf

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
K. v.	Theory	33.60	15.87	—	—	2.24	—	—	34.85	—	—	13.44	100.00
Hauer	XIV	33.51	15.42	—	—	2.58	—	—	34.41	—	—	13.21	99.13
Heddle	Theory	32.35	13.76	2.39	—	5.39	—	0.83	32.34	—	—	12.94	100.00
	LXVIII	32.55	13.95	0.97	—	5.28	0.16	0.79	32.78	0.48	0.06	13.17	100.19
Melville	Theory	31.92	7.54	—	11.25	1.06	—	—	35.46	—	—	12.77	100.00
	CLXII	31.74	6.74	—	11.39	1.23	—	0.18	35.18	0.49 NiO	—	13.04	99.99
Kobell	Theory	32.71	15.44	—	—	6.54	—	—	33.32	—	—	11.99	100.00
	XXII	32.68	14.57	—	—	5.97	0.28	—	33.11	1.02 Resid.	—	12.10	99.73
Pearse	Theory	31.71	12.73	—	3.33	2.11	—	1.12	35.23	—	—	13.75	100.00
	CXLVII	31.31	12.84	—	2.98	2.46	—	0.82	35.02	0.45 NiO	—	13.20	99.08
Pearse	Theory	31.71	12.73	—	3.33	2.11	—	1.12	35.23	—	—	13.75	100.00
	CXLVIII	31.86	13.75	—	2.15	2.31	—	1.27	34.90	0.22 NiO	—	13.98	100.44
Breiden-	Theory	31.83	15.03	—	—	5.30	—	0.82	34.19	0.69	0.46	11.68	100.00
baugh	CXXVI	32.33	14.56	—	—	5.29	—	1.04	33.74	0.87	0.54	12.02	100.39

or the general formula

$$m\,MO \cdot 2\,(5\,R_2O_3 \cdot 22\,SiO_2) \cdot n\,H_2O.$$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Rammels-	Theory	40.85	10.26	8.66	—	8.91	—	0.87	20.43	—	—	10.02	100.00
berg	I	40.88	10.96	9.72	—	8.96	—	0.68	20.00	—	—	10.18	100.38
Field	Theory	31.24	—	18.93	—	39.19	—	—	—	—	—	10.64	100.00
	IX	31.72	—	18.51	—	39.46	—	—	—	—	—	11.02	100.71
Schrauf	Theory	39.38	13.70	2.39	—	2.68	—	—	28.95	—	—	12.90	100.00
	I	38.88	13.45	3.22	—	2.55	—	0.45	28.57	—	—	12.75	99.87
Garret	Theory	37.77	11.68	—	4.35	2.57	—	4.01	25.17	1.06NiO	—	13.39	100.00
	CXLIII	37.66	11.82	—	3.60	2.50	—	4.11	24.98	0.67NiO	—	13.58	98.92
Paltauf	Theory	38.24	12.56	3.48	—	3.13	—	—	29.55	4.09	2.69	6.26	100.00
	LXXXVI	38.04	12.62	2.53	—	2.93	0.51Fl	0.48	29.45	4.17	2.73	6.25	99.71
Hawes	Theory	33.76	11.08	3.07	—	24.86	—	0.72	16.37	—	—	10.14	100.00
	VIII	33.24	11.07	2.26	—	25.11	0.41	1.11	16.51	—	0.25	9.91	99.87
„	Theory	33.76	11.08	3.07	—	24.86	—	0.72	16.37	—	—	10.14	100.00
	IX	33.68	10.84	2.86	—	24.33	0.38	0.73	16.52	—	0.33	10.02	99.69
Liebe	Theory	31.61	9.77	3.83	—	23.70	—	—	19.83	—	—	11.21	100.00
	VI	31.25	10.03	3.47	—	23.52	—	—	19.73	—	—	11.37	99.37
„	Theory	31.63	12.22	—	—	21.56	—	—	22.52	—	—	12.07	100.00
	III	31.69	12.22	—	—	21.26	—	—	22.05	—	—	12.47	99.69
„	Theory	31.63	12.22	—	—	21.56	—	—	22.52	—	—	12.07	100.00
	IV	31.38	11.89	—	—	22.72	—	—	22.91	—	—	10.91	99.81
„	Theory	31.63	12.22	—	—	21.56	—	—	22.52	—	—	12.07	100.00
	VII	31.56	12.08	—	—	21.61	—	—	22.44	—	—	11.78	99.47
Piccard	Theory	33.94	13.12	—	—	6.49	—	—	33.94	—	—	12.51	100.00
	XLII	33.54	13.39	—	—	6.62	—	—	33.56	—	—	12.38	99.49
Heddle	Theory	32.46	7.52	—	7.49	1.77	—	4.13	32.46	—	—	14.17	100.00
	LXIV	32.31	7.50	—	7.89	2.08	—	3.83	32.15	—	—	14.25	100.01
v. Fellen-	Theory	33.73	11.73	2.04	—	1.84	—	—	37.32	—	—	13.04	100.00
berg	XLV	33.97	11.66	2.49	—	1.81	—	—	37.60	—	—	13.57	101.10
Liebe	Theory	30.14	11.64	—	—	26.70	—	—	21.24	—	—	10.28	100.00
	I	30.27	11.16	—	—	26.94	—	—	21.22	—	—	10.20	99.79

J. Orthochlorites of the type

$$\hat{R} \cdot \hat{Si} \cdot \hat{R} = 6\, R_2O_3 \cdot 6\, SiO_2$$

				Source
95	$18\,MO \cdot 2\,(6\,Fe_2O_3 \cdot 6\,SiO_2) \cdot 22\,H_2O$	$18\,MO = 18\,FeO$	Cronstedtite	Kuttenberg

K. Orthochlorites of the type

$$\bar{\bar{Si}} \cdot \hat{R} \cdot \hat{R} \cdot \overline{Si} = 6\, R_2O_3 \cdot 10\, SiO_2$$

				Source
96	$16\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 28\,H_2O$	$16\,MO = 16\,MgO$ $12\,R_2O_3 = 9.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	Orthochlorite	Unionville
97	$16\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 30\,H_2O$	$16\,MO = 16\,MgO$ $12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	"	"
98	$20\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 24\,H_2O$	$20\,MO = 18\,FeO \cdot 1.5\,MgO \cdot 0.5\,CaO$ $12\,R_2O_3 = 8.5\,Al_2O_3 \cdot 3.5\,Fe_2O_3$	Aphrosiderite	Königshain
99	$23\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 26\,H_2O$	$23\,MO = 17\,MgO \cdot 5\,FeO \cdot 1\,K_2O$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Orthochlorite	Unionville
100	$23\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 26\,H_2O$	$23\,MO = 17\,MgO \cdot 5\,FeO \cdot 1\,K_2O$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	"	"
101	$26\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 30\,H_2O$	$26\,MO = 24\,FeO \cdot 2\,MgO$ $12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	Thuringite	Harper's Ferry
102	$26\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 30\,H_2O$	$26\,MO = 24\,FeO \cdot 2\,MgO$ $12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	"	Schmiedefeld
103	$26\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 30\,H_2O$	$26\,MO = 23.5\,FeO \cdot 2\,MgO \cdot 0.5\,Na_2O$ $12\,R_2O_3 = 8\,Al_2O_3\ \ 4\,Fe_2O_3$	"	Harper's Ferry
104	$26\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 30\,H_2O$	$26\,MO = 23.5\,FeO \cdot 2\,MgO \cdot 0.5\,Na_2O$ $12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	"	"
105	$27\,MO \cdot 2(6\,Fe_2O_3 \cdot 10\,SiO_2) \cdot 24\,H_2O$	$27\,MO = 19\,FeO \cdot 7\,MgO \cdot 1\,MnO$	Cronstedtite	Přibram
106	$27\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 30\,H_2O$	$27\,MO = 23.5\,FeO \cdot 2.5\,MgO \cdot 1\,MnO$ $12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	Thuringite	Hot Springs
107	$28\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 32\,H_2O$	$28\,MO = 28\,FeO$ $12\,R_2O_3 = 9.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	"	Zirmsee
108	$29\,MO \cdot 2(6\,Fe_2O_3 \cdot 10\,SiO_2) \cdot 32\,H_2O$	$29\,MO = 20\,FeO \cdot 7\,MgO \cdot 2\,MnO$	Cronstedtite	Přibram
109	$29\,MO \cdot 2(6\,Fe_2O_3 \cdot 10\,SiO_2) \cdot 32\,H_2O$	" " " "	"	"
110	$30\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 28\,H_2O$	$30\,MO = 23\,MgO \cdot 6\,FeO \cdot 1\,MnO$ $12\,R_2O_3 = 10.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	Klementite	Vielsalm
111	$30\,MO \cdot 2(6Al_2O_3 \cdot 10\,SiO_2) \cdot 32\,H_2O$	$30\,MO = 27.5\,FeO \cdot 1\,MgO \cdot 1\,Na_2O \cdot 0.5\,MnO$	Daphnite	Penzance
112	$30\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 32\,H_2O$	$30\,MO = 21.5\,FeO \cdot 8.5\,MgO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Orthochlorite	Düllen
113	$30\,MO \cdot 2(6\,Fe_2O_3 \cdot 10\,SiO_2) \cdot 38\,H_2O$	$30\,MO = 23\,FeO \cdot 6\,MgO \cdot 1\,MnO$	Cronstedtite	Přibram
114	$34\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 32\,H_2O$	$34\,MO = 22\,MgO \cdot 12\,FeO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Orthochlorite	Washington, D.C.
115	$36\,MO \cdot 2(6\,R_2O_3 \cdot 10\,SiO_2) \cdot 28\,H_2O$	$36\,MO = 15.5\,MgO \cdot 16\,FeO \cdot 0.5\,MnO$ $12\,R_2O_3 = 10.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	"	Steeles Mount, N.C.

or the general formula

$m\ MO \cdot 2\ (6\ R_2O_3 \cdot 6\ SiO_2) \cdot n\ H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Rosam	Theory	16.62	—	44.32	—	29.92	—	—	—	—	—	9.14	100.00
	VI	17.34	—	43.05	—	30.27	0.16	—	—	—	—	9.18	100.00

or the general formula

$m\ MO \cdot 2\ (6\ R_2O_3 \cdot 10\ SiO_2) \cdot n\ H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
König	Theory	32.32	26.10	10.77	—	—	—	—	17.25	—	—	13.56	100.00
	CXXXIV	32.80	26.07	9.80	—	—	—	—	17.70	—	—	13.75	100.12
,,	Theory	31.29	21.27	16.67	—	—	—	—	16.68	—	—	14.09	100.00
	CXXXIII	31.35	21.58	14.17	—	—	—	—	16.67	—	—	14.45	98.22
Woitschach	Theory	27.01	19.52	12.60	—	29.17	—	0.63	1.35	—	—	9.72	100.00
	V	27.06	19.56	11.71	—	28.91	—	0.38	1.18	—	—	9.73	98.53
Gintl	Theory	29.38	27.47	3.92	—	8.81	—	—	16.64	2.32	—	11.46	100.00
	CXXXVIII	29.89	30.87	—	—	9.17	—	—	17.53	2.41	0.83	11.60	102.30
,,	Theory	29.38	27.47	3.92	—	8.81	—	—	16.64	2.32	—	11.46	100.00
	CXXXIX	29.90	27.59	3.12	—	9.17	—	—	17.10	2.33	0.58	11.51	101.30
Keyser	Theory	23.98	16.31	12.79	—	34.53	—	—	1.60	—	—	10.79	100.00
	VI	23.21	15.59	13.89	—	34.51	—	0.36	1.26	0.08	0.41	10.59	99.97
Smith	Theory	23.98	16.31	12.79	—	34.53	—	—	1.60	—	—	10.79	100.00
	III	23.55	15.63	13.79	—	34.20	—	—	1.47	—	—	10.57	99.21
,,	Theory	24.01	16.32	12.80	—	33.85	—	—	1.60	—	0.62	10.80	100.00
	VII	23.58	16.85	14.33	—	33.20	0.09	—	1.52	—	0.46	10.45	100.48
,,	Theory	24.01	16.32	12.80	—	33.85	—	—	1.60	—	0.62	10.80	100.00
	VIII	23.52	16.08	—	—	32.18	—	—	1.68	—	—	10.48	—
Ludwig	Theory	22.76	—	36.43	—	25.96	1.35	—	5.31	—	—	8.19	100.00
	V	22.21	—	37.49	—	25.28	1.20	—	5.23	—	—	8.27	99.68
Smith	Theory	23.77	16.17	12.68	—	33.29	1.41	—	1.98	—	—	10.70	100.00
	IX	23.70	16.54	12.13	—	33.14	1.16	—	1.85	0.32 (K_2O,Na_2O)		10.90	99.74
Gintl	Theory	23.25	18.77	7.75	—	39.06	—	—	—	—	—	11.17	100.00
	V	22.65	18.92	8.12	—	38.49	—	—	—	—	—	10.58	98.96
Steinmann	Theory	21.59	—	34.55	—	25.91	2.55	—	5.04	—	—	10.37	100.00
	I	22.45	—	58.85 (Fe_2O_3+FeO)		—	2.89	—	5.08	—	—	10.70	99.97
Kobell	Theory	21.59	—	34.55	—	25.91	2.55	—	5.04	—	—	10.37	100.00
	II	22.45	—	35.35	—	27.11	2.89	—	5.08	—	—	10.70	103.58
Klement	Theory	27.04	24.13	5.41	—	9.73	1.69	—	20.73	—	—	11.36	100.00
	I	27.13	24.70	5.84	—	9.72	1.98	—	20.52	—	—	11.35	101.24
R.v.Zeynek	Theory	23.46	23.92	—	—	38.70	0.67	—	0.78	—	1.21	11.26	100.00
	I	23.62	22.26	—	—	38.97	0.98	0.29	1.09	0.28	1.10	11.16	99.75
v. Gümbel	Theory	24.26	22.69	3.23	—	31.30	—	—	6.87	—	—	11.65	100.00
	V	23.56	22.35	4.25	—	30.43	—	0.23	6.75	0.10 Alk	—	11.49	99.16
Janowsky	Theory	20.78	—	33.26	—	28.70	1.23	—	4.15	—	—	11.88	100.00
	IV	21.30	—	32.34	—	29.23	1.25	—	4.51	—	—	11.90	100.53
Clarke and Schneider	Theory	24.99	23.36	3.33	—	17.99	—	—	18.33	—	—	12.00	100.00
	CL	25.40	22.80	2.86	—	17.77	0.25	—	19.09	—	—	12.21	100.38
Genth	Theory	24.78	22.12	4.96	—	23.79	1.14	—	12.81	—	—	10.40	100.00
	CLXI	24.90	21.77	4.60	—	24.21	1.15	—	12.78	—	—	10.59	100.00

				Source
116	$36\,MO \cdot 2\,(6\,R_2O_3 \cdot 10\,SiO_2)$ $\cdot 32\,H_2O$	$36\,MO = 22\,MgO \cdot 14\,FeO$ $12\;R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Orthochlorite	Lude
117	$36\,MO \cdot 2\,(6\,R_2O_3 \cdot 10\,SiO_2)$ $\cdot 32\,H_2O$	$36\,MO = 22\,MgO \cdot 14\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	,,
118	$37\,MO \cdot 2\,(6\,R_2O_3 \cdot 10\,SiO_2)$ $\cdot 34\,H_2O$	$37\,MO = 25\,MgO \cdot 12\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Chester, Mass.
119	$38\,MO \cdot 2\,(6\,Al_2O_3 \cdot 10\,SiO_2)$ $\cdot 32\,H_2O$	$38\,MO = 28\,MgO \cdot 10\,FeO$	,,	,,

L. Orthochlorites of the type

$$\hat{Si} \cdot \hat{R} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 12\,SiO_2$$

				Source
120	$18\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 28\,H_2O$	$18\,MO = 15\,MgO \cdot 2.5\,K_2O \cdot 0.5\,Na_2O$ $12\,R_2O_3 = 9\,Al_2O_3 \cdot 3\,Fe_2O_3$	Orthochlorite	Culsagee Mine, N.C.
121	$24\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 26\,H_2O$	$24\,MO = 18.5\,FeO \cdot 5\,MnO \cdot 0.5\,CaO$ $12\,R_2O_3 = 8.5\,Al_2O_3 \cdot 3.5\,Fe_2O_3$	Strigovite	Striegau
122	$25\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 24\,H_2O$	$25\,MO = 10\,FeO \cdot 10.5\,MgO \cdot 3.5\,CaO$ $\cdot 1\,Na_2O;\ 12\,R_2O_3 = 8\,Al_2O_3 \cdot 4\,Fe_2O_3$	Chloropite	Weidesgrün
123	$25\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 30\,H_2O$	$25\,MO = 22\,MgO \cdot 2.5\,FeO \cdot 0.5\,CaO$ $12\,R_2O_3 = 7\,Al_2O_3 \cdot 5\,Fe_2O_3$	Delessite	La Grève bei Mielin
124	$26\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 40\,H_2O$	$26\,MO = 22\,FeO \cdot 2\,MgO \cdot 2\,CaO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Orthochlorite	Striegau
125	$28\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 22\,H_2O$	$28\,MO = 6.5\,MgO \cdot 20\,FeO \cdot 1\,K_2O$ $\cdot 0.5\,MnO;\ 12\,R_2O_3 = 9\,Al_2O_3 \cdot 3Fe_2O_3$	,,	Waldsassen
126	$29\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_3)$ $\cdot 34\,H_2O$	$29\,MO = 18.5\,MgO \cdot 10\,FeO \cdot 0.5\,CaO$ $12\,R_2O_3 = 9.5\,Al_2O_3 \cdot 2.5\,Fe_2O_3$	Delassite	Planitz bei Zwickau
127	$30\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 28\,H_2O$	$30\,MO = 17.5\,FeO \cdot 11.5MgO \cdot 0.5\,K_2O$ $\cdot 0.5\,Na_2O;\ 12R_2O_3 = 7.5\,Al_2O_3 \cdot 4.5Fe_2O_3$	Chloropite	Schwarzenbach
128	$30\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 30\,H_2O$	$30MO = 9\,FeO \cdot 18.5\,MgO \cdot 1\,CaO \cdot 1\,Na_2O$ $\cdot 05\,K_2O;\ 12\,R_2O_3 = 7\,Al_2O_3 \cdot 5\,Fe_2O_3$	,,	Lippertsgrün
129	$30\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot 32\,H_2O$	$30\,MO = 20\,FeO \cdot 10\,MgO$	Orthochlorite	Taszopáták
130	$35\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot 24\,H_2O$	$35\,MO = 33.5\,FeO \cdot 1.5\,MgO$	Aphrosiderite	Weilburg
131	$36\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 30\,H_2O$	$36\,MO = 29.5\,FeO \cdot 6.5\,MgO$ $12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	,,	Striegau
132	$36\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2)$ $\cdot 40\,H_2O$	$36\,MO = 30\,FeO \cdot 6\,MgO$	Chamosite	Windgällen
133	$38\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 32\,H_2O$	$38\,MO = 16\,MgO \cdot 22\,FeO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Orthochlorite	Muttershausen
134	$38\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 32\,H_2O$	$38\,MO = 16\,MgO \cdot 22\,FeO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	,,	Balduinstein
135	$38\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 34\,H_2O$	$38\,MO = 34\,MgO \cdot 4\,FeO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	,,	Unionville, Pa.
136	$38\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 34\,H_2O$	$38\,MO = 34\,MgO \cdot 4\,FeO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	,,	,,
137	$38\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2)$ $\cdot 34\,H_2O$	$38\,MO = 31\,FeO \cdot 6.5\,MgO \cdot 0.5\,CaO$ $12\,R_2O_3 = 10\,Al_2O_3 \cdot 2\,Fe_2O_3$	Metachlorite	Büchenberge b. Elbingerode

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Heddle	Theory	24.40	23.86	1.62	—	20.50	—	—	17.90	—	—	11.72	100.00
	LXXIII	23.92	22.98	1.11	—	19.54	0.28	2.45	17.26	—	—	11.78	99.32
„	Theory	24.40	23.86	1.62	—	20.50	—	—	17.90	—	—	11.72	100.00
	LXXIV	24.66	23.19	0.64	—	20.58	0.29	0.40	17.79	—	—	12.12	99.67
Obermayer	Theory	24.35	23.80	1.62	—	17.53	—	—	20.29	—	—	12.41	100.00
	CXXIII	23.84	25.22	2.81	—	17.06	—	—	19.83	—	—	11.90	100.66
Pasani	Theory	24.79	25.29	—	—	14.88	—	—	23.14	—	—	11.90	100.00
	CXXI	24.00	25.90	—	—	14.80	—	—	22.70	—	—	11.90	99.30

or the general formula

$$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Chatard	Theory	34.32	21.81	11.41	—	—	—	—	14.26	5.58	0.74	11.98	100.00
	CLVII	34.22	21.53	12.41	—	0.12 (Ni,Co)O		—	14.46	5.70	0.51	11.85	100.80
Websky	Theory	28.53	17.17	11.09	—	26.39	6.99	0.55	—	—	—	9.28	100.00
	I	28.43	16.60	11.43	—	26.21	7.25	0.37	0.36	—	—	9.31	99.96
Loretz	Theory	30.46	17.26	13.54	—	15.24	—	4.16	8.89	—	1.31	9.14	100.00
	II	30.56	16.57	13.02	—	15.51	—	4.14	8.97	0.36	1.18	9.08	99.39
Delesse	Theory	31.43	15.58	17.46	—	3.93	—	0.60	19.21	—	—	11.79	100.00
	I	31.07	15.47	17.54	—	4.07	—	0.46	19.14	—	—	11.55	99.30
Traube	Theory	27.75	22.61	—	1.54	30.52	—	2.15	1.54	—	—	13.89	100.00
	X	27.12	22.40	—	2.13	30.19	—	2.23	1.54	—	—	13.45	99.06
v. Gümbel	Theory	27.99	19.41	9.33	—	27.99	0.69	—	5.05	1.83	—	7.71	100.00
	IV	27.50	18.15	10.80	—	28.02	0.60	—	5.13	1.66	0.44	7.50	99.80
Delesse	Theory	29.33	19.74	8.14	—	14.67	—	0.57	15.07	—	—	12.48	100.00
	III	29.45	18.25	8.17	—	15.12	—	0.45	15.32	—	—	12.57	99.33
Loretz	Theory	27.55	14.63	13.77	—	24.12	—	—	8.80	0.90	0.59	9.64	100·00
	I	27.10	14.64	14.80	—	23.85	—	—	8.78	0.52	0.56	9.69	99.94
„	Theory	28.44	14.10	15.80	—	12.80	—	1.10	14.64	0.92	1.22	10.98	100.00
	III	29.10	14.31	14.87	—	13.27	—	1.00	15.08	0.60	1.09	10.77	100.09
K. v. Hauer	Theory	28.35	24.10	—	—	28.35	—	—	7.87	—	—	11.33	100.00
	XVII	28.02	23.84	—	—	28.60	—	—	8.09	—	—	11.45	100.00
Sandberger	Theory	25.86	21.98	—	—	43.32	—	—	1.08	—	—	7.76	100.00
	I	26.45	21.25	—	—	44.24	—	—	1.06	—	—	7.74	100.74
Rammelsberg	Theory	25.24	17.88	5.61	—	37.24	—	—	4.56	—	—	9.47	100.00
	IV	24.78	18.69	6.45	—	36.17	Trace	—	4.52	—	—	9.09	99.70
C. Schmidt	Theory	24.90	21.16	—	—	37.35	—	—	4.14	—	—	12.45	100.00
	II	25.23	19.97	—	—	37.51	—	—	4.39	—	—	12.90	100.00
Erlenmeyer	Theory	26.07	20.32	2.90	—	28.69	—	—	11.59	—	—	10.43	100.00
	VI	25.72	20.69	4.01	—	27.79	—	—	11.70	—	—	10.05	99.96
„	Theory	26.07	20.32	2.90	—	28.69	—	—	11.59	—	—	10.43	100.00
	VII	25.99	—	4.13	—	27.60	—	—	11.93	—	—	10.13	—
Chatard	Theory	28.68	22.35	3.13	—	5.75	—	—	27.90	—	—	12.19	100.00
	CXXXV	29.43	22.08	1.47	—	5.64	—	—	28.46	—	—	12.40	99.42
„	Theory	28.68	22.35	3.13	—	5.75	—	—	27.90	—	—	12.19	100.00
	CXXXVI	29.59	22.18	1.33	—	5.77	—	—	28.54	—	—	12.40	99.81
Zeynek	Theory	24.36	17.25	5.41	—	37.75	—	0.47	4.40	—	—	10.36	100.00
	II	24.29	17.85	4.64	—	37.85	—	0.57	4.26	0.09	0.30	10.19	100.04

				Source
138	$39\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$39\,MO = 25\,FeO \cdot 14\,MgO$	Ortho-chlorite	Grabener Wiesen
139	$39\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$39\,MO = 25\,MgO \cdot 12\,FeO \cdot 1\,K_2O \cdot 1\,Na_2O$; $12\,R_2O_3 = 10.5Al_2O_3 \cdot 1.5Fe_2O_3$	,,	Fuschertal
140	$39\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	$39\,MO = 19\,MgO \cdot 20\,FeO$ $12\,R_2O_3 = 10.5\,Al_2O_3 \cdot 1.5\,Fe_2O_3$	,,	Zillerthal
141	$39\,MO \cdot 2\,(6\,Fe_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	$39\,MO = 31.5\,FeO \cdot 6.5\,MgO \cdot 1\,MnO$	Cronstedtite	Příbram
142	$40\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	$40\,MO = 19\,MgO \cdot 21\,FeO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	Ortho-chlorite	Zillertal
143	$41\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 40\,H_2O$	$41\,MO = 37\,MgO \cdot 4\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Culsagee Mine, N.C.
144	$41\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 40\,H_2O$	$41\,MO = 37\,MgO \cdot 4\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	,,
145	$41\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 40\,H_2O$	$41\,MO = 37\,MgO \cdot 4\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	,,
146	$42\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	$42\,MO = 21\,FeO \cdot 19\,MgO \cdot 1\,K_2O \cdot 0.5\,MnO \cdot 0.5\,CaO$	,,	Ben Derag
147	$42\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 38\,H_2O$	$42\,MO = 26\,MgO \cdot 16\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Aacherkoppe
148	$43\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$43\,MO = 25\,MgO \cdot 18\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	St. Gotthard
149	$43\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$43\,MO = 32\,MgO \cdot 10.5\,FeO \cdot 0.5\,MnO$ $12\,R_2O_3 = 11\,Al_2O_3 \cdot 1\,Fe_2O_3$	,,	Portsoy
150	$43\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	$43\,MO = 32\,MgO \cdot 11\,FeO$	,,	Zillertal
151	$43\,MO \cdot 2(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	,, ,, ,,	,,	,,
152	$43\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 38\,H_2O$	$43\,MO = 22\,MgO \cdot 20\,FeO \cdot 1\,CaO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Massa-schlucht
153	$43\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 40\,H_2O$	$43\,MO = 19.5\,MgO \cdot 22\,FeO \cdot 1\,CaO \cdot 0.5MnO$; $12R_2O_3 = 11.5Al_2O_3 \cdot 0.5Fe_2O_3$	,,	Girdleness
154	$44\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$44\,MO = 22\,MgO \cdot 22\,FeO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Zillertal
155	$44\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$44\,MO = 40\,MgO \cdot 4\,FeO$	,,	Grochau
156	$46\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 24\,H_2O$	$46\,MO = 20.5\,MgO \cdot 25.5\,FeO$	,,	Guistberg
157	$48\,MO \cdot 2\,(6\,R_2O_3 \cdot 12\,SiO_2) \cdot 38\,H_2O$	$48\,MO = 33\,MgO \cdot 14\,FeO \cdot 0.5\,MnO \cdot 0.5CaO$; $12R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5Fe_2O_3$	,,	Fethaland
158	$51\,MO \cdot 2\,(6\,Al_2O_3 \cdot 12\,SiO_2) \cdot 32\,H_2O$	$51\,MO = 31\,MgO \cdot 16\,FeO \cdot 2\,CaO \cdot 1\,K_2O \cdot 0.5\,MnO \cdot 0.5\,Na_2O$	,,	Craig an Lochan

M. Orthochlorites of the type

$$\overline{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \overline{Si} = 6\,R_2O_3 \cdot 16\,SiO_2$$

				Source
159	$32\,MO \cdot 2\,(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 36\,H_2O$	$32\,MO = 30\,MgO \cdot 2\,FeO$ $12\,R_2O_3 = 6.5\,Al_2O_3 \cdot 1\,Fe_2O_3 \cdot 4.5Cr_2O_3$	Ortho-chlorite	Norrbotten
160	$41\,MO \cdot 2\,(6\,R_2O_3 \cdot 16\,SiO_2) \cdot 52\,H_2O$	$41\,MO = 29.5\,MgO \cdot 10\,FeO \cdot 1.5\,CaO$ $12\,R_2O_3 = 11.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Delessite	Dumbuek

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
K. v.	Theory	25.82	21.93	—	—	32.26	—	—	10.03	—	—	9.96	100.00
Hauer	XVIII	26.08	20.27	—	—	32.91	—	—	10.00	—	—	10.06	99.32
Vuylsteke	Theory	26.75	19.89	4.46	—	16.06	—	—	18.57	1.74	1.15	11.38	100.00
	XIX	27.03	20.07	4.72	—	16.47	—	—	18.90	1.22	0.72	11.78	100.91
Klement	Theory	25.72	19.13	4.29	—	25.72	—	—	13.58	—	—	11.56	100.00
	XXIX	25.84	19.58	4.42	—	25.99	—	—	13.57	—	—	11.34	100.74
Damour	Theory	21.89	—	29.06	—	34.33	1.07	—	3.93	—	—	9.81	100.00
	III	21.39	—	29.08	—	33.52	1.01	—	4.02	—	—	9.76	98.78
Klement	Theory	25.52	19.89	2.84	—	26.80	—	—	13.46	—	—	11.49	100.00
	XXX	25.84	19.58	2.13	—	28.05	—	—	13.57	—	—	11.34	100.51
Genth	Theory	27.79	22.64	1.55	—	5.56	—	—	28.56	—	—	13.90	100.00
	CLIII	27.56	22.75	2.56	—	5.43	—	—	28.47	0.30 (Mn, Ni, Co)O		13.80	100.87
Chatard	Theory	27.79	22.64	1.55	—	5.56	—	—	28.56	—	—	13.90	100.00
	CLIV	27.28	22.11	2.50	—	5.43	—	—	28.38	0.41 (Mn, Ni, Co)O		14.50	100.57
,,	Theory	27.79	22.64	1.55	—	5.56	—	—	28.56	—	—	13.90	100.00
	CLV	27.17	22.35	2.71	—	5.43	—	—	27.73	0.26 (Mn, Ni, Co)O		14.36	100.00
Heddle	Theory	25.11	21.34	—	—	26.35	0.62	0.40	13.25	1.63	—	11.30	100.00
	LXXI	24.72	21.57	0.62	—	26.16	0.47	0.45	12.86	1.73	0.05	10.89	99.52
Jacobs	Theory	25.86	21.07	1.43	—	20.68	—	—	18.68	—	—	12.28	100.00
	VIII	25.53	20.49	1.68	0.08	20.85	0.15 TiO_2	0.06	18.60	0.07	0.09	12.26	99.86
Rammels-	Theory	25.71	20.95	1.43	P_2O_5	23.14	—	—	17.85	—	—	10.92	100.00
berg	XXXIV	25.12	22.26	1.09	—	23.11	—	—	17.41	—	—	10.70	99.69
Heddle	Theory	26.59	20.72	2.95	—	13.96	0.83	—	23.64	—	—	11.31	100.00
	LXXVI	26.71	20.42	3.47	—	13.99	0.73	—	23.90	—	—	11.17	100.39
Kobell	Theory	26.74	22.72	—	—	14.71	—	—	23.77	—	—	12.06	100.00
	XXVI	26.51	21.81	—	—	15.00	—	—	22.83	—	—	12.00	98.15
,,	Theory	26.74	22.72	—	—	14.71	—	—	23.77	—	—	12.06	100.00
	XXVII	27.32	20.69	—	—	15.23	0.47	—	24.89	—	—	12.00	100.60
Fellen-	Theory	25.03	20.39	1.39	—	25.03	—	0.97	15.29	—	—	11.90	100.00
berg	XXXV	24.85	20.70	1.00	—	25.00	—	0.60	15.31	0.45 TiO_2		12.05	99.96
Heddle	Theory	24.53	19.97	1.36	—	27.04	0.60	0.95	13.28	—	—	12.27	100.00
	LXXVII	24.77	20.16	1.38	—	27.38	0.61	0.90	13.34	—	—	12.05	100.59
Egger	Theory	25.28	20.59	1.42	—	27.80	—	—	15.45	—	—	9.48	100.00
	XXVIII	26.02	20.16	1.07	—	28.08	—	0.44	15.50	—	—	9.65	100.92
Bock	Theory	27.88	23.70	—	—	5.58	—	—	30.99	—	—	11.85	100.00
	IX	28.20	24.56	—	—	5.27	—	—	30.94	—	—	12.15	101.12
Igelström	Theory	25.03	21.28	—	—	31.92	—	—	14.25	—	—	7.52	100.00
	LXXXIII	25.00	20.60	—	—	32.00	—	—	14.30	—	—	7.60	99.50
Heddle	Theory	24.96	20.33	1.39	—	17.48	0.61	0.49	22.88	—	—	11.86	100.00
	LXX	24.30	20.86	3.57	—	16.72	0.55	0.50	22.20	—	—	11.55	100.25
,,	Theory	24.39	20.73	—	—	19.51	0.59	1.96	21.00	1.59	0.52	9.77	100.00
	LXXII	24.29	21.15	0.10	—	18.74	0.80	1.66	21.03	1.29	0.56	10.08	99.70

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 16\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Sanderson	Theory	35.42	12.23	2.95	12.64	2.66	—	—	22.14	—	—	11.96	100.00
	LXXXVII	34.49	12.40	3.14	13.46	3.28	—	—	21.83	—	—	11.85	100.45
Heddle	Theory	31.52	19.25	1.31	—	11.82	—	1.37	19.36	—	—	15.37	100.00
	VII	32.01	18.87	1.18	—	12.09	Trace	1.39	19.64	—	—	15.46	100.64

				Source
161	$48 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 32 H_2O$	$48 MO = 43 MgO \cdot 5 FeO$	Ortho-chlorite	Brosso
162	$48 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 40 H_2O$	$48 MO = 48 MgO$ $12 R_2O_3 = 10 Al_2O_3 \cdot 1.5 Fe_2O_3 \cdot 0.5 Cr_2O_3$	,,	Westchester, Pa.
163	$48 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 40 H_2O$	$48 MO = 48 MgO$ $12 R_2O_3 = 10 Al_2O_3 \cdot 1.5 Fe_2O_3 \cdot 0.5 Cr_2O_3$	,,	,,
164	$49 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 46 H_2O$	$49 MO = 47 MgO \cdot 2 FeO$ $12 R_2O_3 = 11.5 Al_2O_3 \cdot 0.5 Fe_2O_3$	,,	Zoutpansberge
165	$51 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 40 H_2O$	$51 MO = 26 MgO \cdot 21 FeO \cdot 4 MnO$ $12 R_2O_3 = 9.5 Al_2O_3 \cdot 2.5 Fe_2O_3$	,,	Dannemora
166	$51 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 40 H_2O$	$51 MO = 26 MgO \cdot 21 FeO \cdot 4 MnO$ $12 R_2O_3 = 9.5 Al_2O_3 \cdot 2.5 Fe_2O_3$	,,	,,
167	$52 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 44 H_2O$	$52 MO = 23 MgO \cdot 29 FeO$	,,	St. Christophe
168	$53 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 46 H_2O$	$53 MO = 46 MgO \cdot 7 FeO$	,,	Blair Athol
169	$53 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 46 H_2O$	$53 MO = 52.5 MgO \cdot 0.5 FeO$ $12 R_2O_3 = 11 Al_2O_3 \cdot 1 Fe_2O_3$	,,	Achmatowsk
170	$55 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 50 H_2O$	$55 MO = 51 MgO \cdot 2 FeO \cdot 2 Na_2O$ $12 R_2O_3 = 11 Al_2O_3 \cdot 0.5 Fe_2O_3 \cdot 0.5 Cr_2O_3$	,,	Westchester, Pa
171	$55 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 40 H_2O$	$55 MO = 52 MgO \cdot 2 FeO \cdot 1 CaO$ $12 R_2O_3 = 11 Al_2O_3 \cdot 0.5 Fe_2O_3 \cdot 0.5 Cr_2O_3$	,,	,,
172	$55 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 48 H_2O$	$55 MO = 53 MgO \cdot 2 FeO$ $12 R_2O_3 = 9 Al_2O_3 \cdot 2 Fe_2O_3 \cdot 1 Cr_2O_3$	,,	,,
173	$56 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 42 H_2O$	$56 MO = 53 MgO \cdot 3 FeO$ $12 R_2O_3 = 10 Al_2O_3 \cdot 2 Cr_2O_3$	,,	Itkul Sea
174	$56 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 44 H_2O$	$56 MO = 54 MgO \cdot 2 FeO$	,,	Schischimsker Berge
175	$56 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 44 H_2O$	$56 MO = 54 MgO \cdot 2 FeO$	,,	,,
176	$56 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 44 H_2O$	,, ,, ,,	,,	,,
177	$58 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 40 H_2O$	$58 MO = 29 MgO \cdot 29 FeO$	,,	Glacier d'Argentiéres
178	$58 MO \cdot 2(6 R_2O_3 \cdot 16 SiO_2) \cdot 42 H_2O$	$58 MO = 58 MgO$ $12 R_2O_3 = 11 Al_2O_3 \cdot 1 Fe_2O_3$	,,	Fluß Iremel
179	$61 MO \cdot 2(6 Al_2O_3 \cdot 16 SiO_2) \cdot 52 H_2O$	$61 MO = 54 MgO \cdot 3.5 FeO \cdot 2 CaO \cdot 1.5 K_2O$	,,	Texas, Pa.

N. Orthochlorites of the type

$$\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} - \hat{Si} = 6 R_2O_3 \cdot 18 SiO_2$$

				Source
180	$18 MO \cdot 2(6 R_2O_3 \cdot 18 SiO_2) \cdot 42 H_2O$	$18 MO = 10.5 MgO \cdot 4.5 CaO \cdot 3 FeO$ $12 R_2O_3 = 7 Fe_2O_3 \cdot 5 Al_2O_3$	Hullite	Carnmoney Hill
181	$23 MO \cdot 2(6 R_2O_3 \cdot 18 SiO_2) \cdot 34 H_2O$	$23 MO = 21,5 FeO \cdot 1.5 Na_2O$ $12 R_2O_3 = 9 Fe_2O_3 \cdot 3 Al_2O_3$	Melanolite	Milk-Row Quarry, Mass.
182	$36 MO \cdot 2(6 Al_2O_3 \cdot 18 SiO_2) \cdot 26 H_2O$	$36 MO = 20 MgO \cdot 16 FeO$	Epiphanite	Wermland

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Damour	Theory	33.10	21.10	—	—	6.21	—	—	29.64	—	—	9.95	100.00
	LVI	33.67	20.37	—	—	6.37	—	—	29.49	—	—	10.10	100.00
Graw	Theory	32.56	17.30	4.07	1.29	—	—	—	32.56	—	—	12.22	100.00
	CXXVIII	31.34	17.47	3.85	1.69	—	—	—	33.44	—	—	12.60	100.39
„	Theory	32.56				—	—	—	32.56	—	—	12.22	100.00
	CXXIX	31.78	—	22.71	—	—	—	—	33.64	—	—	12.60	100.73
Yvan Riesen	Theory	31.86	19.47	1.33	—	2.39	—	—	31.21	—	—	13.74	100.00
	CXV	32.38	18.79	0.80	—	2.39	—	—	31.64	—	—	14.15	100.15
Erdmann	Theory	28.05	14.15	5.84	—	22.09	4.15	—	15.19	—	—	10.53	100.00
	LXXX	27.83	14.23	5.34	—	22.53	3.21	—	15.42	0.36	0.27	10.19	99.38
„	Theory	28.05	14.15	5.84	—	22.09	4.15	—	15.19	—	—	10.53	100.00
	LXXXI	27.89	14.30	5.96	—	21.21	5.43	0.43	14.42	0.17	0.23	10.30	100.34
Marignac	Theory	27.65	17.63	—	—	30.07	—	—	13.25	—	—	11.40	100.00
	LIX	26.88	17.52	—	—	29.76	—	—	13.84	—	—	11.33	99.33
Heddle	Theory	30.40	19.38	—	—	7.98	—	—	29.13	—	—	13.11	100.00
	LXVI	30.30	19.40	—	—	8.23	0.37	—	29.10	—	—	13.07	100.47
Ortmann	Theory	31.15	18.19	2.59	—	0.58	—	—	34.05	—	—	13.44	100.00
	XCIV	31.31	18.34	2.10	—	0.77	—	—	34.25	0.06	0.17	13.33	100.33
Schlaepfer	Theory	29.96	17.52	1.25	1.18	2.25	—	—	31.85	—	1.94	14.05	100.00
	CXXXII	30.11	18.31	1.16	1.55	2.11	0.31 Li_2O	—	31.89	0.37	1.99	14.14	101.94
Neminar	Theory	30.98	18.11	1.29	1.23	2.32	—	0.90	33.56	—	—	11.61	100.00
	CXXX	31.08	18.85	1.55	1.09	2.33	—	0.81	33.50	—	—	11.53	100.74
Clarke and Schneider	Theory	29.83	14.26	4.97	2.36	2.24	—	—	32.93	—	—	13.41	100.00
	CXXXI	29.87	14.48	5.52	1.56	1.93	—	—	33.06	0.17 NiO	—	13.60	100.19
Hermann	Theory	30.31	16.09	—	4.81	3.40	—	—	33.45	—	—	11.94	100.00
	CXII	30.58	15.94	—	4.99	3.32	—	—	33.45	—	—	12.05	100.33
Herzog N.v Leuchtenberg	Theory	30.77	19.62	—	—	2.31	—	—	34.61	—	—	12.69	100.00
	XCVIII	30.60	19.63	—	—	2.02	—	—	34.41	—	—	12.76	99.42
„	Theory	30.77	19.62	—	—	2.31	—	—	34.61	—	—	12.69	100.00
	XCIX	30.33	19.85	—	—	2.43	—	0.11	34.64	—	—	12.73	100.09
Lagorio	Theory	30.77	19.62	—	—	2.31	—	—	34.61	—	—	12.69	100.00
	C	30.61	19.52	0.30	—	2.53	—	—	34.20	—	—	12.53	99.69
Brun	Theory	27.00	17.21	—	—	29.36	—	—	16.31	—	—	10.13	100.00
	XLIX	26.60	18.02	—	—	29.67	—	—	15.85	—	—	9.98	100.12
Hermann	Theory	30.58	17.87	2.55	—	—	—	—	36.96	—	—	12.04	100.00
	CX	30.80	17.27	1.37	—	—	—	—	37.08	—	—	12.30	98.82
Pearse	Theory	28.47	18.15	—	—	3.73	1.66	—	32.02	2·09	—	13.88	100.00
	CXL	28.62	18.37	—	0.37 NiO	3.73	1.45	—	32.13	1.97	—	14.02	100.00

or the general formula

$m\,MO \cdot 2\,(6\,R_2O_3 \cdot 18\,SiO_2) \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Hardmann	Theory	39.75	9.39	20.61	—	3.98	—	4.64	7.73	—	—	13.90	100.00
	I	39.44	10.35	20.72	—	3.70	Trace	4.48	7.47	—	—	13.62	99.78
Wurtz	Theory	35.07	4.97	23.38	—	25.14	—	—	—	—	1.51	9.93	100.00
	II	35.24	4.48	23.13	—	25.09	—	—	—	—	1.85	10.21	100.00
Igelström	Theory	37.22	21.09	—	—	19.85	—	—	13.78	—	—	8.06	100.00
	I	37.10	21.13	—	—	20.00	Trace	—	14.03	—	—	7.83	100.09

				Source
183	$44\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 42\ H_2O$	$44\ MO = 44\ FeO$ $12\ R_2O_3 = 10\ Al_2O_3 \cdot 2\ Fe_2O_3$	Chamosite	Schmiedefeld
184	$48\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$48\ MO = 30\ MgO \cdot 17\ FeO \cdot 1\ MnO$ $12\ R_2O_3 = 10\ Al_2O_3 \cdot 2\ Fe_2O_3$	Orthochlorite	Cape Wrath
185	$48\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 60\ H_2O$	$48\ MO = 34.5\ MgO \cdot 11.5\ FeO \cdot 2\ CaO$ $12\ R_2O_3 = 11.5\ Al_2O_3 \cdot 0.5\ Fe_2O_3$	Delessite	Bowling Quarry, Dumbarton
186	$49\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 56\ H_2O$	$49\ MO = 32.5\ MgO \cdot 15\ FeO \cdot 1.5\ CaO$ $12\ R_2O_3 = 10.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	,,	Long Craig, Dumbarton
187	$49\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 44\ H_2O$	$49\ MO = 48\ MgO \cdot 1\ FeO$ $12\ R_2O_3 = 11.5\ Al_2O_3 \cdot 0.5\ Fe_2O_3$	Orthochlorite	Čkyn
188	$52\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 52\ H_2O$	$52\ MO = 50\ MgO \cdot 1\ CaO \cdot 1\ FeO$ $12\ R_2O_3 = 11\ Al_2O_3 \cdot 1\ Fe_2O_3$	,,	Markich
189	$54\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 30\ H_2O$	$54\ MO = 53\ MgO \cdot 1\ CaO$ $12\ R_2O_3 = 10.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	,,	Schischimsker Berge
190	$54\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 30\ H_2O$	$54\ MO = 53\ MgO \cdot 1\ CaO$ $12\ R_2O_3 = 10.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	,,	,,
191	$57\ MO \cdot 2\ (6\ Al_2O_3 \cdot 18\ SiO_2) \cdot 46\ H_2O$	$57\ MO = 53\ MgO \cdot 4\ FeO$	,,	,,
192	$58\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 42\ H_2O$	$58\ MO = 50\ MgO \cdot 8\ CaO$ $12\ R_2O_3 = 10.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3$	,,	,,
193	$58\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 46\ H_2O$	$58\ MO = 58\ MgO$ $12R_2O_3 = 8.5Al_2O_3 \cdot 1.5Fe_2O_3 \cdot 2Cr_2O_3$	,,	Ufaléjsk
194	$58\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 46\ H_2O$	$58\ MO = 58\ MgO$ $12\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3 \cdot 2\ Cr_2O_3$	,,	,,
195	$58\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 46\ H_2O$	$58\ MO = 58\ MgO$ $12\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5Fe_2O_3 \cdot 2\ Cr_2O_3$	,,	,,
196	$58\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 46\ H_2O$	$58\ MO = 58\ MgO$ $12\ R_2O_3 = 8.5\ Al_2O_3 \cdot 1.5\ Fe_2O_3 \cdot 2\ Cr_2O_3$	,,	Bilimbajewsk
197	$59\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$59\ MO = 59\ MgO$ $12\ R_2O_3 = 10\ Al_2O_3 \cdot 2\ Fe_2O_3$	,,	Texas, Pa.
198	$59\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$59\ MO = 59\ MgO$ $12\ R_2O_3 = 10\ Al_2O_3 \cdot 2\ Fe_2O_3$	,,	Willimantic, Conn.
199	$60\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$60\ MO = 55\ MgO \cdot 4\ FeO \cdot 1\ CaO$ $12\ R_2O_3 = 11.5\ Al_2O_3 \cdot 0.5\ Fe_2O_3$	,,	Kariaet, Greenland
200	$62\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 52\ H_2O$	$62\ MO = 54\ MgO \cdot 2\ FeO \cdot 4\ CaO \cdot 1\ K_2O \cdot 1\ Na_2O$; $12\ R_2O_3 = 9\ Al_2O_3 \cdot 3\ Cr_2O_3$	,,	Unst
201	$62\ MO \cdot 2\ (6\ Al_2O_3 \cdot 18\ SiO_2) \cdot 46\ H_2O$	$62\ MO = 61.5\ MgO \cdot 0.5\ FeO$	,,	Mauléon
202	$62\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$62\ MO = 62\ MgO$ $12\ R_2O_3 = 9\ Al_2O_3 \cdot 3\ Fe_2O_3$	,,	Achmatowsk
203	$62\ MO \cdot 2\ (6\ R_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$62\ MO = 62\ MgO$ $12\ R_2O_3 = 9\ Al_2O_3 \cdot 3\ Fe_2O_3$	,,	,,
204	$63\ MO \cdot 2\ (6\ Al_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$63\ MO = 53\ MgO \cdot 8\ FeO \cdot 2\ CaO$	,,	Kariaet, Greenland
205	$64\ MO \cdot 2\ (6\ Al_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	$64\ MO = 60\ MgO \cdot 4\ FeO$	,,	Achmatowsk
206	$64\ MO \cdot 2\ (6\ Al_2O_3 \cdot 18\ SiO_2) \cdot 48\ H_2O$	,, ,, ,,	,,	,,

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Loretz	Theory	29.08	13.79	4.33	—	42.62	—	—	—	—	—	10.18	100.00
	IV	29.00	13.00	6.00	—	42.00	—	—	—	—	—	10.00	100.00
Heddle	Theory	31.49	14.87	4.67	—	17.85	1.03	—	17.49	—	—	12.60	100.00
	LXVIII	31.03	14.85	5.73	—	17.42	1.00	0.36	17.42	—	—	12.48	100.29
"	Theory	31.70	17.22	1.17	—	12.16	—	1.64	20.25	—	—	15.86	100.00
	VI	32.00	17.33	1.19	—	12.45	—	1.57	20.42	—	—	15.45	100.41
"	Theory	31.11	15.43	3.46	—	15.55	—	1.21	18.73	—	—	14.51	100.00
	VIII	30.93	15.32	3.16	—	15.31	0.38	1.38	18.65	—	—	14.69	99.82
Gintl	Theory	34.85	18.93	1.29	—	1.16	—	—	30.97	—	—	12.78	100.00
	XIII	35.31	18.28	1.26	—	0.83	—	—	31.61	—	—	13.26	100.55
van	Theory	33.21	17.23	2.46	—	1.11	—	0.86	30.74	—	—	14.39	100.00
Weryecke	II	32.84	17.34	3.29	—	1.04	—	0.75	30.48	—	—	14.44	100.18
Komonen	Theory	35.12	17.40	3.90	—	—	—	0.90	33.92	—	—	8.75	100.00
	XCV	34.99	17.15	3.39	—	—	—	1.42	34.49	—	—	8.56	100.00
"	Theory	35.12	17.40	3.90	—	—	—	0.90	33.92	—	—	8.75	100.00
	XCVI	34.23	16.31	3.33	—	—	—	1.75	35.36	—	—	8.68	99.66
Hermann	Theory	32.62	18.49	—	—	4.35	—	—	32.02	—	—	12.52	100.00
	XCVII	32.35	18.00	—	—	4.37	—	—	32.29	—	—	12.50	99.51
Clarke and	Theory	32.36	16.05	3.59	—	—	—	6.71	29.96	—	—	11.33	100.00
Schneider	CI	32.27	16.05	4.26	—	0.28	—	6.21	29.75	—	—	11.47	100.29
Herzog von	Theory	32.14	12.90	3.57	4.53	—	—	—	34.54	—	—	12.32	100.00
Leuchtenberg	CII	33.12	13.56	2.29	4.19	—	—	—	35.77	—	—	12.65	101.58
"	Theory	32.14	12.90	3.57	4.53	—	—	—	34.54	—	—	12.32	100.00
	CIII	32.35	13.29	2.00	4.19	—	—	—	35.04	—	—	12.62	99.49
N. v. Zinn	Theory	32.14	12.90	3.57	4.53	—	—	—	34.54	—	—	12.32	100.00
	CIV	33.31	12.60	2.30	4.04	—	—	—	35.62	—	—	12.62	100.49
"	Theory	32.14	12.90	3.57	4.53	—	—	—	34.54	—	—	12.32	100.00
	CVI	32.50	13.20	2.30	4.00	—	—	—	35.60	—	—	12.60	100.30
Hermann	Theory	32.13	15.15	4.76	—	—	—	—	35.10	—	—	12.86	100.00
	CXLI	31.82	15.10	4.06	0.90	0.25 NiO	—	—	35.24	—	—	12.75	100.12
Burton	Theory	32.13	15.15	4.76	—	—	—	—	35.10	—	—	12.86	100.00
	CXLIX	31.86	15.80	4.77	—	—	—	0.30	34.30	—	—	12.72	99.75
Hammer-	Theory	31.76	16.95	1.19	—	4.23	—	0.82	32.35	—	—	12.70	100.00
schlag	CXVI	30.34	16.86	1.86	—	4.53	—	0.61	31.82	—	0.37	12.70	99.09
Heddle	Theory	30.19	12.83	—	6.38	2.01	—	3.13	30.19	1.32	0.87	13.08	100.00
	LXIII	29.89	12.93	—	5.97	1.96	—	3.54	29.93	1.16	0.97	13.27	99.62
Delesse	Theory	31.99	18.13	—	—	1.18	—	—	36.44	—	—	12.26	100.00
	LVIII	32.10	18.50	—	—	0.60	—	—	36.70	—	—	12.10	100.00
Struve	Theory	31.29	13.30	6.95	—	—	—	—	35.93	—	—	12.53	100.00
	XCII	31.64	13.54	5.83	—	—	—	0.05	36.20	—	—	12.74	100.00
"	Theory	31.29	13.30	6.95	—	—	—	—	35.93	—	—	12.53	100.00
	XCIII	31.52	13.96	6.12	—	—	—	0.05	35.68	—	—	12.67	100.00
Janowsky	Theory	30.62	17.34	—	—	8.16	—	1.59	30.04	—	—	12.25	100.04
	CXVII	30.32	17.90	—	—	7.71	—	1.28	29.88	—	—	12.28	99.37
Kobell	Theory	31.14	17.64	—	—	4.16	—	—	34.60	0.85(Resd.)		12.46	100.00
	LXXXIX	31.14	17.14	—	—	3.85	0.53	—	34.40	—	—	12.20	100.11
Varrentrapp	Theory	31.14	17.64	—	—	4.16	—	—	34.60	0.85(Resd.)		12.46	100.00
	XC	30.38	16.97	—	—	4.37	—	—	33.97	—	—	12.63	98.32

O. Orthochlorites of the type
$\bar{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \bar{R} = 8\,R_2O_3 \cdot 12\,SiO_2$

				Source
207	$40\,MO \cdot 2(8\,Fe_2O_3 \cdot 12\,SiO_2) \cdot 44\,H_2O$	$40\,MO = 40\,FeO$	Cronstedtite	Cornwall
208	$41\,MO \cdot 2(8\,Al_2O_3 \cdot 12\,SiO_2) \cdot 40\,H_2O$	$41\,MO = 31\,FeO \cdot 10\,MgO$	Thuringite	Lake Superior

P. Orthochlorites of the type
$\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} = 9\,R_2O_3 \cdot 12\,SiO_2$

				Source
209	$16\,MO \cdot 2(9\,Al_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$16\,MO = 14\,MgO \cdot 1\,CaO \cdot 1\,FeO$	Rumpfite	St. Michael
210	$28\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 30\,H_2O$	$28\,MO = 25\,FeO \cdot 3\,MgO$ $18\,R_2O_3 = 15\,Al_2O_3 \cdot 3\,Fe_2O_3$	Aphrosiderite	Weilburg
211	$30\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 42\,H_2O$	$30\,MO = 28\,FeO \cdot 2\,MgO$ $18\,R_2O_3 = 7{\cdot}5\,Fe_2O_3 \cdot 10.5\,Al_2O_3$	Thuringite	Schmiedefeld
212	$33\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 36\,H_2O$	$33\,MO = 31\,FeO \cdot 2\,MgO$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,Fe_2O_3$	„	„
213	$37\,MO \cdot 2(9\,Al_2O_3 \cdot 12\,SiO_2) \cdot 34\,H_2O$	$37\,MO = 24\,MgO \cdot 13\,FeO$	Orthochlorite	Chester, Mass.
214	$40\,MO \cdot 2(9\,Fe_2O_3 \cdot 12\,SiO_2) \cdot 46\,H_2O$	$40\,MO = 40\,FeO$	Cronstedtite	Cornwall

New Formulæ for

The following analyses of the minerals

A. $\bar{R} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 6\,SiO_2$,

B. $\bar{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \bar{R} = 8\,R_2O_3 \cdot 12\,SiO_2$,

A. Tourmalines of the type
$\bar{R} \cdot \hat{Si} \cdot \bar{R} = 5\,R_2O_3 \cdot 6\,SiO_2$

			Source	Analyst *
1	$4\,RO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 4\,H_2O$	$4\,MO = 0.5\,MnO \cdot 1.5\,Li_2O{\cdot}1\,Na_2O{\cdot}0.5\,K_2O \cdot 0.5\,H_2O$; $20\,R_2O_3 = 16\,Al_2O_3 \cdot 4\,B_2O_3$	Elba	Rammelsberg
2	$4\,RO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 9\,H_2O$	$4\,MO = 0.5\,CaO \cdot 2\,Li_2O \cdot 1.5\,Na_2O$ $20\,R_2O_3 = 15.5\,Al_2O_3 \cdot 4.5\,B_2O_3$	Rumford	Riggs
3	$5\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 4\,H_2O$	$5\,MO = 1\,MnO{\cdot}0.5\,CaO{\cdot}1.5\,Li_2O{\cdot}1.5\,Na_2O{\cdot}0.5\,K_2O$; $20\,R_2O_3 = 15.5\,Al_2O_3 \cdot 4.5\,B_2O_3$	Paris	Rammelsberg
4	$5\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 5\,H_2O$	$5\,MO = 1\,MnO{\cdot}0.5\,CaO{\cdot}1.5\,MgO \cdot 1\,Li_2O \cdot 1\,Na_2O$; $20\,R_2O_3 = 16\,Al_2O_3 \cdot 4\,B_2O_3$	Schaitauka	„
5	$5\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 5\,H_2O$	$5\,MO = 1.5\,FeO{\cdot}0.5\,MgO{\cdot}1\,Li_2O \cdot 1.5\,MnO \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 15\,Al_2O_3{\cdot}5\,B_2O_3$	Elba	„
6	$5\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$5\,MO = 0.5\,MnO{\cdot}0.5\,CaO{\cdot}2\,Li_2O \cdot 1\,Na_2O \cdot 1\,K_2O$; $20\,R_2O_3 = 15.5\,Al_2O_3 \cdot 4.5\,B_2O_3$	Schütten-hofen	Scharizer
7	$6\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 7\,H_2O$	$6\,MO = 1.5\,FeO{\cdot}1.5\,MnO{\cdot}0.5\,CaO{\cdot}0.5\,Li_2O \cdot 2\,Na_2O$; $20\,R_2O_3 = 15\,Al_2O_3 \cdot 5\,B_2O_3$	Brazil	Jannasch and Calb
8	$6\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$6\,MO = 1\,FeO \cdot 1\,MnO \cdot 0.5\,CaO \cdot 2\,Li_2O \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 14.5\,Al_2O_3{\cdot}5.5\,B_2O_3$	„	Riggs

* See references on p. 441

or the general formula

$m\ MO \cdot 2\ (8\ R_2O_3 \cdot 12\ SiO_2) \cdot n\ H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Flight	Theory	18.77	—	33.36	—	37.54	—	—	—	—	—	10.33	100.00
	VIII	18.55	—	32.75	—	38.57	—	—	—	—	—	10.13	100.00
Penfield and Sperry	Theory	22.28	25.25	—	—	35.25	—	—	6.18	—	—	11.14	100.00
	X	22.35	25.14	—	—	34.39	—	—	6.41	—	—	11.25	99.54

or the general formula

$m\ MO \cdot 2\ (9\ R_2O_3 \cdot 12\ SiO_2) \cdot n\ H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Firtsch	Theory	31.48	40.12	—	—	1.57	—	1.22	12.23	—	—	13.38	100.00
	I	30.75	41.66	—	—	1.61	—	0.89	12.09	—	—	13.12	100.12
Sand-berger	Theory	24.36	25.89	8.13	—	30.45	—	—	2.03	—	—	9.14	100.00
	III	24.63	25.25	8.50	—	30.61	—	—	1.82	—	—	9.19	100.00
L. Smith	Theory	21.94	16.32	18.28	—	30.72	—	—	1.22	—	—	11.52	100.00
	I	22.05	16.40	17.66	—	30.78	—	—	0.89	0.14 ($K_2O \cdot Na_2O$)		11.44	99.36
Rammels-berg	Theory	21.74	18.48	14.47	—	34.30	—	—	1.21	—	—	9.78	100.00
	II	22.35	18.39	14.86	—	34.34	—	—	1.25	—	—	9.81	101.00
L. Smith	Theory	24.90	31.71	—	—	16.21	—	—	16.60	—	—	10.58	100.00
	CXXII	25.06	30.70	—	—	16.50	—	—	16.41	—	—	10.62	99.29
Flight	Theory	17.94	—	35.87	—	35.87	—	—	—	—	—	10.32	100.00
	VII	17.47	—	36.76	—	36.31	—	0.09	—	—	—	10.09	100.72

the Tourmaline Group

of this group conform to the following types:

C. $\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} = 9\ R_2O_3 \cdot 12\ SiO_2$.

or the general formula

$m\ MO \cdot 4\ (5\ R_2O_3 \cdot 6\ SiO_2) \cdot n\ H_2O$

	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	Li_2O	Na_2O	K_2O	H_2O	Fl	Total	Loss on Ignition
Theory	39.76	7.71	45.06	0.00	0.00	0.00	0.98	0.00	0.00	1.24	1.71	1.30	2.24	0.00	100.00	—
XX	38.85	9.52	44.05	0.00	0.00	0.00	0.92	0.00	0.20	1.22	2.00	1.30	2.41	0.70	101.17	—
Theory	39.15	8.54	42.99	0.00	0.00	0.00	0.00	0.76	0.00	1.63	2.53	0.00	4.40	0.00	100.00	—
LXVIII	38.07	9.99	42.24	0.00	0.26	0.00	0.35	0.56	0.07	1.59	2.18	0.44	4.26	0.28	100.29	—
Theory	39.01	8.52	42.83	0.00	0.00	0.00	1.92	0.76	0.00	1.22	2.52	1.27	1.95	0.00	100.00	—
LXII	38.19	9.97	42.63	0.00	0.00	0.00	1.94	0.45	0.39	1.17	2.60	0.68	2.00	1.18	101.20	—
Theory	39.00	7.57	44.20	0.00	0.00	0.00	1.92	0.76	1.62	0.81	1.68	0.00	2.44	0.00	100.00	—
XXXI	38.26	9.29	43.97	0.00	0.00	0.00	1.53	0.62	1.62	0.48	1.53	0.21	2.49	0.70	100.70	—
Theory	38.97	9.45	41.41	0.00	0.97	0.00	2.88	0.00	0.54	0.82	2.52	0.00	2.44	0.00	100.00	—
XIX	37.71	9.99	41.89	0.00	1.38	0.00	2.51	0.00	0.41	0.74	2.40	0.34	2.60	0.50	100.47	—
Theory	37.94	8.28	41.66	0.00	0.00	0.00	0.94	0.74	0.00	1.58	1.64	2.48	4.74	0.00	100.00	—
VIII	38.49	8.25	41.49	0.00	0.35	0.00	0.60	1.82	0.00	1.68	1.32	2.14	4.61	0.43	100.00	—
Theory	37.63	9.13	39.98	0.00	2.82	0.00	2.78	0.73	0.00	0.40	3.24	0.00	3.29	0.00	100.00	—
XLII	37.05	9.09	40.03	0.00	2.36	0.00	2.35	0.47	0.32	0.60	3.18	Trace	3.23	1.15	99.83	—
Theory	38.18	10.18	39.22	0.00	1.91	0.00	1.88	0.74	0.00	1.59	2.47	0.00	3.83	0.00	100.00	—
XXXVIII	37.39	10.29	39.65	0.00	2.29	0.00	1.47	0.49	0.00	1.71	2.42	0.25	3.63	0.32	99.91	—

			Source	Analyst
9	$6\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 9\,H_2O$	$6\,MO = 1\,FeO \cdot 1\,MnO \cdot 0.5\,CaO \cdot 2\,Li_2O \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 14.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Auburn	Riggs
10	$6\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 9\,H_2O$	$6\,MO = 2\,FeO \cdot 0.5\,CaO \cdot 2\,Li_2O \cdot 1.5\,Na_2O$ $20\,R_2O_3 = 14\,Al_2O_3 \cdot 6\,B_9O_3$	,,	,,
11	$7\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 5\,H_2O$	$7\,MO = 1.5\,FeO \cdot 0.5\,CaO \cdot 4\,MgO \cdot 1\,Na_2O$ $20\,R_2O_3 = 11.5\,Al_2O_3 \cdot 5.5\,B_2O_3 \cdot 3\,Cr_2O_3$	N. Issetsk	Cossa
12	$7\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 6\,H_2O$	$7\,MO = 1.5\,FeO \cdot 1.5\,MnO \cdot 0.5\,CaO \cdot 1.5\,Li_2O \cdot 2\,Na_2O$; $20\,R_2O_3 = 14.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Brazil	Jannasch and Calb
13	$7\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$7\,MO = 1.5\,FeO \cdot 1.5\,MnO \cdot 0.5\,CaO \cdot 2\,Li_2O \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 14.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	,,	Riggs
14	$7\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$7\,MO = 3.5\,FeO \cdot 1.5\,Li_2O \cdot 2\,Na_2O$ $20\,R_2O_3 = 14.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Rumford	,,
15	$8\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 4\,H_2O$	$8\,MO = 3\,FeO \cdot 0.5\,MnO \cdot 1\,MgO \cdot 2\,Li_2O \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 14\,Al_2O_3 \cdot 6\,B_2O_3$	Brazil	Rammelsberg
16	$8\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 9\,H_2O$	$8\,MO = 4\,FeO \cdot 0.5\,MnO \cdot 1.5\,Li_2O \cdot 2\,Na_2O$ $20\,R_2O_3 = 14.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Auburn	Riggs
17	$8\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 10\,H_2O$	$8\,MO = 2.5\,FeO \cdot 1.5\,MnO \cdot 2\,Li_2O \cdot 0.5\,K_2O \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 15.5\,Al_2O_3 \cdot 4.5\,B_2O_3$	Schütten-hofen	Scharizer
18	$10\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 2\,H_2O$	$10\,MO = 3\,FeO \cdot 0.5\,MnO \cdot 4\,MgO \cdot 0.5\,K_2O \cdot 2\,Na_2O$; $20\,R_2O_3 = 14\,Al_2O_3 \cdot 6\,B_2O_3$	M. Bisch	Sommerland
19	$10\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 3\,H_2O$	$10\,MO = 7.5\,FeO \cdot 1.5\,MgO \cdot 1\,Na_2O$ $20\,R_2O_3 = 14\,Al_2O_3 \cdot 6\,B_2O_3$	Saar	Rammelsberg
20	$10\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 5\,H_2O$	$10\,MO = 6.5\,FeO \cdot 1\,MgO \cdot 0.5\,MnO \cdot 1\,Li_2O \cdot 1\,Na_2O$; $20\,R_2O_3 = 13\,Al_2O_3 \cdot 7\,B_2O_3$	Goshen	,,
21	$10\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$10\,MO = 8\,FeO \cdot 1\,MgO \cdot 1\,Na_2O$ $20\,R_2O_3 = 13\,Al_2O_3 \cdot 7\,B_2O_3$	Auburn	Riggs
22	$10\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$10\,MO = 7\,FeO \cdot 1.5\,MgO \cdot 1.5\,Na_2O$ $20\,R_2O_3 = 14.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Paris	,,
23	$10\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$10\,MO = 7.5\,FeO \cdot 1.5\,MgO \cdot 1\,Na_2O$ $20\,R_2O_3 = 13.5\,Al_2O_3 \cdot 6.5\,B_2O_3$	Alabaschka	Jannasch and Calb
24	$12\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 2\,H_2O$	$12\,MO = 8.5\,FeO \cdot 0.5\,MnO \cdot 2\,MgO \cdot 0.5\,Na_2O \cdot 0.5\,H_2O$; $20\,R_2O_3 = 12\,Al_2O_3 \cdot 8\,B_2O_3$	,,	Rammelsberg
25	$12\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 6\,H_2O$	$12\,MO = 8.5\,FeO \cdot 1.5\,MgO \cdot 2\,Na_2O$ $20\,R_2O_3 = 14\,Al_2O_3 \cdot 6\,B_2O_3$	Mursinka	Jannasch and Calb
26	$12\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$12\,MO = 4.5\,FeO \cdot 5.5\,MgO \cdot 0.5\,CaO \cdot 1.5\,Na_2O$; $20\,R_2O_3 = 13.5\,Al_2O_3 \cdot 6.5\,B_2O_3$	Stony	Riggs
27	$12\,MO \cdot 4(5\,R_2O_3 \cdot 6\,SiO_2) \cdot 8\,H_2O$	$12\,MO = 6\,FeO \cdot 4\,MgO \cdot 2\,Na_2O$ $20\,R_2O_3 = 13\,Al_2O_3 \cdot 6\,B_2O_3 \cdot 1\,Fe_2O_3$	Piedra	Jannasch and Calb

B. Tourmalines of the type
$\overline{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \overline{R} = 8\,R_2O_3 \cdot 12\,SiO_2$

			Source	Analyst
28	$7\,MO \cdot 2(8\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$7\,MO = 3\,FeO \cdot 0.5\,CaO \cdot 1\,MgO \cdot 0.5\,K_2O \cdot 2\,Na_2O$; $16\,R_2O_3 = 14\,Al_2O_3 \cdot 2\,B_2O_3$	Waldheim	Sauer
29	$13\,MO \cdot 2(8\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$13\,MO = 2\,FeO \cdot 1\,CaO \cdot 9\,MgO \cdot 1\,Na_2O$ $16\,R_2O_3 = 11.5\,Al_2O_3 \cdot 4.5\,B_2O_3$	Monroe	Rammelsberg
30	$14\,MO \cdot 2(8\,R_2O_3 \cdot 12\,SiO_2) \cdot 5\,H_2O$	$14\,MO = 5\,FeO \cdot 0.5\,MnO \cdot 0.5\,CaO \cdot 6.5\,MgO \cdot 1.5\,Na_2O$; $16\,R_2O_3 = 11\,Al_2O_3 \cdot 5\,B_2O_3$	Elba	,,
31	$14\,MO \cdot 2(8\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$14\,MO = 4.5\,FeO \cdot 1.5\,CaO \cdot 7\,MgO \cdot 1\,Na_2O$ $16\,R_2O_3 = 10\,Al_2O_3 \cdot 4.5\,B_2O_3 \cdot 1.5\,Fe_2O_3$	Tamatave	Jannasch and Calb

	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	Li_2O	Na_2O	K_2O	H_2O	Fl	Total	Loss on Ignition
Theory	38.02	10.14	39.03	0.00	1.90	0.00	1.87	0.73	0.00	1.58	2.45	0.00	4.28	0.00	100.00	—
LXIV	38.14	10.25	39.60	0.30	1.38	0.00	1.38	0.43	Trace	1.34	2.36	0.27	4.16	0.62	100.23	4.09
Theory	38.16	11.10	37.84	0.00	3.82	0.00	0.00	0.74	0.00	1.59	2.46	0.00	4.29	0.00	100.00	—
LXV	37.85	10.55	37.73	0.42	3.88	0.00	0.51	0.49	0.04	1.34	2.16	0.62	4.18	0.62	100.39	—
Theory	36.91	9.84	30.06	11.70 Cr_2O_3	2.77	0.00	0.00	0.72	4.10	1.59	0.00	0.00	2.31	0.00	100.00	—
XXXII	36.79	9.51	30.56	10.86 Cr_2O_3	2.91	0.00	Trace	0.72	4.47	1.36	0.00	Trace	2.25	0.65	100.08	—
Theory	37.68	10.05	38.69	0.00	2.82	0.00	2.79	0.73	0.00	1.17	3.25	0.00	2.82	0.00	100.00	—
XLI	37.40	10.74	39.02	0.00	2.35	0.00	2.57	0.60	0.20	1.33	3.59	0.29	3.08	0.98	102.15	—
Theory	37.48	9.99	38.49	0.00	2.81	0.00	2.77	0.73	0.00	1.56	2.42	0.00	3.75	0.00	100.00	—
XXXIX	36.91	9.87	38.13	0.31	3.19	0.00	2.22	0.38	0.04	1.61	2.70	0.28	3.64	0.14	99.42	3.62
Theory	37.21	9.93	38.23	0.00	6.51	0.00	0.00	0.00	0.00	1.19	3.21	0.00	3.72	0.00	100.00	—
LXIX	36.53	10.22	38.10	0.00	6.43	0.00	0.32	0.34	0.00	0.95	2.86	0.38	3.52	0.16	99.81	3.31
Theory	37.86	11.02	37.55	0.00	5.68	0.00	0.93	0.00	1.05	1.58	2.44	0.00	1.89	0.00	100.00	—
XXXVI	38.06	10.09	37.81	0.00	5.83	0.00	1.13	0.00	0.92	1.30	2.21	0.42	2.23	0.70	100.70	—
Theory	36.39	9.70	37.37	0.00	7.28	0.00	0.90	0.00	0.00	1.14	3.13	0.00	4.09	0.00	100.00	—
LXVI	36.26	9.94	36.68	0.15	7.07	0.00	0.72	0.17	0.16	1.05	2.88	0.44	4.05	0.71	100.28	—
Theory	35.99	7.85	39.50	0.00	4.50	0.00	2.66	0.00	0.00	1.50	2.33	1.17	4.50	0.00	100.00	—
VII	36.38	8.12	39.77	0.00	4.17	0.00	2.83	0.00	0.00	1.54	1.93	0.93	4.29	0.00	100.00	—
Theory	36.87	10.74	36.56	0.00	5.53	0.00	0.91	0.00	4.10	0.00	3.17	1.20	0.92	0.00	100.00	—
XXXIV	36.86	10.56	36.72	0.00	5.66	0.00	0.66	0.34	3.92	0.00	3.57	1.11	1.16	0.61	101.17	—
Theory	35.97	10.47	35.67	0.00	13.49	0.00	0.00	0.00	1.50	0,00	0.55	0.00	1.35	0.00	100.00	—
X	36.11	11.64	35.46	0.00	13.17	0.00	0.28	0.00	1.52	0.00	0.98	0.09	1.26	0.41	100.92	—
Theory	36.18	12.28	33.31	0.00	11.75	0.00	0.89	0.00	1.00	0.75	1.56	0.00	2.26	0.00	100.00	—
LVIII	36.22	10.65	33.35	0.00	11.95	0.00	1.25	0.00	0.63	0.84	1.75	0.40	2.21	0.82	100.07	—
Theory	35.04	10.20	34.76	—	14.02	—	—	—	0.97	—	1.51	—	3.50	—	100.00	—
LXVII	34.99	9.63	33.96	—	14.23	—	0.06	0.15	1.01	Trace	2.01	0.34	3.62	0.00	100.00	2.17
Theory	35.09	9.34	36.04	—	12.28	—	0.00	0.00	1.46	0.00	2.27	—	3.50	—	100.00	—
LXIII	35.03	9.02	34.44	1.13	12.10	—	0.08	0.24	1.81	0.07	2.03	0.25	3.69	0.00	99.89	2.30
Theory	35.32	11.14	33.78	—	13.25	—	—	—	1.47	—	1.52	—	3.53	—	100.00	—
XXVIII	35.41	10.14	33.75	—	13.42	—	Trace	0.17	1.57	—	2.08	0.34	3.41	0.28	100.57	—
Theory	35.76	13.88	30.40	—	15.20	—	0.88	—	1.98	—	0.77	—	1.11	—	100.00	—
XXVII	36.19	12.79	30.40	—	15.59	—	0.54	—	1.88	—	1.04	0.47	1.11	0.76	100.76	—
Theory	34.35	9.99	34.07	—	14.62	—	—	—	1.43	—	2.96	—	2.58	—	100.00	—
XXIX	34.88	8.94	34.58	—	14.40	0.27	0.24	0.20	1.32	—	2.70	0.05	2.87	0.51	100.96	—
Theory	35.30	11.12	33.75	—	7.94	—	—	0.69	5.39	—	2.28	—	3.53	—	100.00	—
XLIV	35.56	10.40	33.38	—	8.43	0.55	0.04	0.53	5.44	Trace	2.16	0.24	3.63	0.00	100.36	2.86
Theory	34.24	9.96	31.53	3.81	10.28	—	—	—	3.81	—	2.95	—	3.42	—	100.00	—
XLIII	34.73	9.64	31.69	3.18	10.14	0.30	0.16	0.36	3.47	—	2.85	0.15	3.44	0.47	100.58	—

or the general formula

$m\,MO \cdot 2\,(8\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O$.

	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	Li_2O	Na_2O	K_2O	H_2O	Fl	Total
Theory	36.64	3.55	36.33	—	5.49	—	—	0.71	10.18	—	3.15	1.19	2.76	—	100.00
III	36.35	4.61	35.76	—	4.78	0.41 SnO_2	—	0.47	10.01	—	3.89	1.22	2.87	—	99.67
Theory	39.38	8.59	32.07	—	3.94	—	—	1.54	9.84	—	1.69	—	2.95	—	100.00
LIII	39.01	8.95	31.18	—	4.07	—	—	1.81	9.90	—	1.82	0.44	2.82	—	100.00
Theory	38.13	9.24	29.71	—	9.53	—	0.94	0.74	6.87	—	2.46	—	2.38	—	100.00
XVII	38.20	9.03	30.02	—	9.93	—	0.58	0.74	6.87	—	2.19	0.25	2.29	0.15	100.15
Theory	37.19	8.12	26.34	6.20	8.37	—	—	2.16	7.23	—	1.60	—	2.80	—	100.00
LXXIII	35.48	9.49	25.83	6.68	7.99	1.22	Trace	2.03	6.90	—	1.92	0.29	2.58	0.33	100.74

			Source	Analyst
32	$15\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 4\ H_2O$	$15\ MO = 4.5\ FeO \cdot 1\ CaO \cdot 8\ MgO \cdot 0.5\ K_2O \cdot 1\ Na_2O$; $16\ R_2O_3 = 11.5\ Al_2O_3 \cdot 4.5\ B_2O_2$	Haddam	Rammelsberg
33	$15\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 6\ H_2O$	$15\ MO = 2\ FeO \cdot 0.5\ CaO \cdot 11\ MgO \cdot 1.5\ Na_2O$ $16\ R_2O_3 = 11.5\ Al_2O_3 \cdot 4.5\ B_2O_3$	Eibenstock	,,
34	$16\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 4\ H_2O$	$16\ MO = 6\ FeO \cdot 0.5\ CaO \cdot 8\ MgO \cdot 0.5\ K_2O \cdot 1\ Na_2O$; $16\ R_2O_3 = 11\ Al_2O_3 \cdot 5\ B_2O_3$	Snarum	,,
35	$16\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 5\ H_2O$	$16\ MO = 0.5\ FeO \cdot 1\ CaO \cdot 14\ MgO \cdot 0.5\ Na_2O$ $16\ R_2O_3 = 11.5\ Al_2O_3 \cdot 4.5\ B_2O_3$	Gouverneur	,,
36	$17\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$17\ MO = 0.5\ FeO \cdot 2\ CaO \cdot 13.5\ MgO \cdot 1\ Na_2O$ $16\ R_2O_3 = 10.5\ Al_2O_3 \cdot 5.5\ B_2O_3$	,,	Riggs
37	$18\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$18\ MO = 0.5\ FeO \cdot 2.5\ CaO \cdot 14\ MgO \cdot 1\ Na_2O$ $16\ R_2O_3 = 11\ Al_2O_3 \cdot 5\ B_2O_3$	Dekabb	,,
38	$19\ MO \cdot 2(8\ R_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$19\ MO = 4.5\ FeO \cdot 2.5\ CaO \cdot 11\ MgO \cdot 1\ Na_2O$ $16\ R_2O_3 = 10\ Al_2O_3 \cdot 6\ B_2O_3$	Pierrepont	,,

C. Tourmalines of the type $\hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} = 9\ R_2O_3 \cdot 12\ SiO_2$

			Source	Analyst
39	$3\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 5\ H_2O$	$3\ MO = 0.5\ MnO \cdot 0.5\ MgO \cdot 1\ Na_2O \cdot 1\ K_2O$ $18\ R_2O_3 = 14\ Al_2O_3 \cdot 4\ B_2O_3$	Rozna	Rammelsberg
40	$5\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 5\ H_2O$	$5\ MO = 2.5\ FeO \cdot 0.5\ MnO \cdot 0.5\ MgO \cdot 1.5\ Na_2O$ $18\ R_2O_3 = 13.5\ Al_2O_3 \cdot 4.5\ B_2O_3$	Campol	Engelmann
41	$8\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 5\ H_2O$	$8\ MO = 3.5\ FeO \cdot 0.5\ MnO \cdot 1.5\ MgO \cdot 1\ Li_2O \cdot 1.5\ Na_2O$; $18\ R_2O_3 = 13.5\ Al_2O_3 \cdot 4.5\ B_2O_3$	Chesterfield	Rammelsberg
42	$10\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 3\ H_2O$	$10\ MO = 5.5\ FeO \cdot 1.5\ MnO \cdot 1\ MgO \cdot 1.5\ Na_2O \cdot 0.5\ H_2O$; $18\ R_2O_3 = 11.5\ Al_2O_3 \cdot 6.5\ B_2O_3$	Sarapulka	,,
43	$10\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 4\ H_2O$	$10\ MO = 5.5\ FeO \cdot 1\ MnO \cdot 1.5\ MgO \cdot 1.5\ Na_2O \cdot 0.5\ K_2O$; $18\ R_2O_3 = 13\ Al_2O_3 \cdot 5\ B_2O_3$	Elba	,,
44	$11\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$11\ MO = 8\ FeO \cdot 0.5\ MgO \cdot 2.5\ Na_2O$ $18\ R_2O_3 = 13.5\ Al_2O_3 \cdot 4.5\ B_2O_3$	Buchw.	Jannasch and Calb
45	$11\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$11\ MO = 9\ MgO \cdot 1.5\ Na_2O \cdot 0.5\ CaO$ $18\ R_2O_3 = 12.5\ Al_2O_3 \cdot 4.5\ B_2O_3 \cdot 1\ Cr_2O_3$	Maryland	Gill
46	$11\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 9\ H_2O$	$11\ MO = 4.5\ FeO \cdot 0.5\ CaO \cdot 4\ MgO \cdot 2\ Na_2O$ $18\ R_2O_3 = 12.5\ Al_2O_3 \cdot 5.5\ B_2O_3$	Tamaya	Schwarz
47	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 3\ H_2O$	$12\ MO = 6.5\ FeO \cdot 0.5\ CaO \cdot 3.5\ MgO \cdot 1\ Na_2O \cdot 0.5\ K_2O$; $18\ R_2O_3 = 12\ Al_2O_3 \cdot 6\ B_2O_3$	Langenb.	Rammelsberg
48	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 3\ H_2O$	$12\ MO = 6.5\ FeO \cdot 0.5\ CaO \cdot 4\ MgO \cdot 1\ Na_2O$ $18\ R_2O_3 = 13\ Al_2O_3 \cdot 5\ B_2O_3$	Krumm	,,
49	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 4\ H_2O$	$12\ MO = 9.5\ FeO \cdot 0.5\ CaO \cdot 1\ MgO \cdot 1\ Na_2O$ $18\ R_2O_3 = 12\ Al_2O_3 \cdot 6\ B_2O_3$	Andreasb.	,,
50	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 4\ H_2O$	$12\ MO = 7.5\ FeO \cdot 0.5\ CaO \cdot 2.5\ MgO \cdot 0.5\ K_2O \cdot 1\ Na_2O$; $18\ R_2O_3 = 11.5\ Al_2O_3 \cdot 6.5\ B_2O_3$	Bovey Tracey	,,
51	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 5\ H_2O$	$12\ MO = 7\ FeO \cdot 0.5\ CaO \cdot 2.5\ MgO \cdot 1\ MnO \cdot 1\ Na_2O$; $18\ R_2O_3 = 12.5\ Al_2O_3 \cdot 5.5\ B_2O_3$	Krumm	,,
52	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 6\ H_2O$	$12\ MO = 1.5\ FeO \cdot 0.5\ CaO \cdot 8.5\ MgO \cdot 0.5\ K_2O \cdot 1\ Na_2O$; $18\ R_2O_3 = 13\ Al_2O_3 \cdot 5\ B_2O_3$	Texas	,,
53	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 8\ H_2O$	$12\ MO = 8\ FeO \cdot 0.5\ CaO \cdot 2\ MgO \cdot 1.5\ Na_2O$ $18\ R_2O_3 = 13\ Al_2O_3 \cdot 5\ B_2O_3$	Brazil	Riggs
54	$12\ MO \cdot 2(9\ R_2O_3 \cdot 12\ SiO_2) \cdot 9\ H_2O$	$12\ MO = 7.5\ FeO \cdot 1\ MnO \cdot 1.5\ MgO \cdot 0.5\ K_2O$ $1.5\ Na_2O$; $18\ R_2O_3 = 14\ Al_2O_3 \cdot 4\ B_2O_3$	Schüttenhofen	Scharizer

	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	Li_2O	Na_2O	K_2O	H_2O	Fl	Total	Loss on Ignition
Theory	37.81	8.25	30.80	—	8.52	—	—	1.47	8.40	—	1.63	1.23	1.89	—	100.00	—
LV	37.50	9.02	30.87	—	8.54	—	—	1.33	8.60	—	1.60	0.73	1.81	—	100.00	—
Theory	38.50	8.40	31.36	—	3.85	—	—	0.75	11.76	—	2.49	—	2.89	—	100.00	—
II	37.75	9.14	30.86	—	4.36	—	—	0.88	11.62	—	2.27	0.30	2.82	—	100.00	—
Theory	37.20	9.02	28.98	—	11.16	—	—	0.72	8.26	—	1.60	1.21	1.85	—	100.00	—
XXV	37.22	9.73	30.00	—	11.16	—	—	0.65	7.94	—	1.13	0.53	1.64	0.55	100.55	—
Theory	38.91	8.49	31.70	—	0.98	—	—	1.51	15.13	—	0.84	—	2.44	—	100.00	—
XLVII	38.85	8.35	31.32	—	1.14	—	—	1.60	14.89	—	1.28	0.26	2.31	—	100.00	—
Theory	38.00	10.14	28.26	—	0.95	—	—	2.96	14.25	—	1.64	—	3.80	—	100.00	—
XLIX	37.39	10.73	27.79	0.10	0.64	1.19	—	2.78	14.09	Trace	1.72	0.16	3.83	Trace	100.42	—
Theory	37.37	9.06	29.12	—	0.93	—	—	3.63	14.54	—	1.61	—	3.74	—	100.00	—
LII	36.88	10.58	28.87	—	0.52	0.12	—	3.70	14.53	Trace	1.39	0.18	3.56	0.50	100.83	—
Theory	36.09	10.50	25.57	—	8.12	—	—	3.51	11.03	—	1.55	—	3.63	—	100.00	—
L	35.61	10.15	25.29	0.44	8.19	0.55	Trace	3.31	11.07	Trace	1.51	0.20	3.34	0.27	99.93	2.69

or the general formula

$m\,MO \cdot 2\,(9\,R_2O_3 \cdot 12\,SiO_2) \cdot n\,H_2O.$

	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	Li_2O	Na_2O	K_2O	H_2O	Fl	Total
Theory	41.75	8.10	41.40	—	—	—	1.03	—	0.58	—	1.80	2.73	2.61	—	100.00
IX	41.16	8.93	41.83	—	—	—	0.95	—	0.61	0.41	1.37	2.17	2.57	1.19	101.19
Theory	40.57	8.86	38.80	—	5.06	—	1.00	—	0.56	—	2.61	—	2.54	—	100.00
XV	39.26	9.40	38.33	—	4.51	—	1.12	—	1.02	—	2.43	0.38	2.41	0.61	99.46
Theory	39.01	8.51	37.29	—	6.83	—	0.96	—	1.63	0.81	2.52	—	2.44	—	100.00
LVII	38.46	9.73	36.80	—	6.38	—	0.78	—	1.88	0.72	2.47	0.47	2.31	0.55	100.55
Theory	38.24	12.06	31.15	—	10.52	—	2.83	—	1.06	—	2.47	—	1.67	—	100.00
XXX	38.30	11.62	31.53	—	10.30	—	2.68	—	1.06	—	2.37	0.33	1.81	0.80	100.80
Theory	37.35	9.06	34.41	—	10.28	—	1.84	—	1.56	—	2.41	1.22	1.87	—	100.00
XVIII	37.14	9.37	34.15	—	10.52	—	1.87	—	1.68	0.32	2.30	0.75	1.90	0.47	100.47
Theory	35.77	7.80	34.20	—	14.30	—	—	—	0.50	—	3.85	—	3.58	—	100.00
XXXIII	35.50	8.34	34.39	—	14.26	—	Trace	Trace	0.51	Trace	3.43	—	3.34	0.77	100.54
Theory	37.83	8.25	33.49	4.00 Cr_2O_3	—	—	—	0.74	9.46	—	2.44	—	3.78	—	100.00
XLV	36.56	8.90	32.58	4.32 Cr_2O_3	0.79 Fe_2O_3	0.09	Trace	0.75	9.47	Trace	2.22	0.13	3.74	0.06	99.70
Theory	36.96	9.86	32.72	—	8.30	—	—	0.72	4.10	—	3.18	—	4.16	—	100.00
XXXV	36.34	10.87	32.22	—	8.31	—	—	0.79	3.92	—	3.14	0.22	3.89	—	99.70
Theory	37.09	10.79	31.53	—	12.06	—	—	0.72	3.61	—	1.60	1.21	1.39	—	100.00
IV	37.24	11.02	31.63	—	11.64	—	—	0.62	3.65	—	1.93	0.82	1.45	—	100.00
Theory	37.05	8.98	34.11	—	12.04	—	—	0.72	4.12	—	1.59	—	1.39	—	100.00
V	36.43	9.82	34.12	—	11.58	—	—	0.44	3.84	—	1.36	0.30	2.11	—	100.00
Theory	36.28	10.56	30.84	—	17.23	—	—	0.71	1.00	—	1.56	—	1.82	—	100.00
I	36.06	11.11	30.34	—	17.40	—	0.11	0.72	0.78	—	1.36	0.58	1.54	0.85	100.85
Theory	36.77	11.60	29.96	—	13.79	—	—	0.71	2.55	—	1.58	1.20	1.84	—	100.00
XXI	37.94	10.72	30.22	—	13.82	—	0.40	0.50	2.62	—	1.39	0.65	1.74	0.45	100.45
Theory	36.42	9.71	32.24	—	12.75	—	1.80	0.70	2.53	—	1.57	—	2.28	—	100.00
XII	36.25	10.27	32.21	—	12.82	—	1.50	0.40	2.32	—	1.43	0.46	2.34	0.64	100.64
Theory	37.81	9.17	34.82	—	2.84	—	—	0.73	8.93	—	1.62	1.23	2.84	—	100.00
XLVII	38.45	8.57	34.56	—	2.98	0.09	—	0.71	9.11	—	2.00	0.73	2.80	—	100.00
Theory	35.68	8.65	32.86	—	14.27	—	—	0.69	1.98	—	2.30	—	3.57	—	100.00
XL	34.63	9.63	32.70	0.31	13.67	—	0.12	0.33	2.13	0.08	2.11	0.24	3.49	0.06	99.52
Theory	34.95	6.78	34.65	—	13.10	—	1.72	—	1.46	—	2.26	1.14	3.94	—	100.00
VI	35.10	7.09	35.10	—	13.36	0.08 SnO_2	1.48	—	0.98	—	1.92	0.88	4.01	—	100.00

			Source	Analyst
55	$13\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 5\,H_2O$	$13\,MO = 7\,FeO \cdot 0.5\,MnO \cdot 3.5\,MgO \cdot 1.5\,Na_2O \cdot 0.5\,H_2O;\ 18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Dekalb	Rammelsberg
56	$13\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$13\,MO = 1.5\,FeO \cdot 10\,MgO \cdot 1.5\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Zillertal	,,
57	$13\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$13\,MO = 4\,FeO \cdot 1\,CaO \cdot 7\,MgO \cdot 1\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	St. Gotthard	,,
58	$13\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$13\,MO = 1.5\,FeO \cdot 0.5\,CaO \cdot 10\,MgO \cdot 1\,Na_2O$ $18\,R_2O_3 = 12.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Orford	,,
59	$13\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 8\,H_2O$	$13\,MO = 2\,FeO \cdot 0.5\,CaO \cdot 9\,MgO \cdot 1.5\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Monroe	Riggs
60	$14\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 4\,H_2O$	$14\,MO = 0.5\,FeO \cdot 1\,CaO \cdot 11\,MgO \cdot 1.5\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Dobrawa	Rammelsberg
61	$14\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$14\,MO = 2.5\,FeO \cdot 1\,CaO \cdot 9\,MgO \cdot 1.5\,Na_2O$ $18\,R_2O_3 = 13\,Al_2O_3 \cdot 5\,B_2O_3$	Godhaab	,,
62	$14\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 7\,H_2O$	$14\,MO = 3\,FeO \cdot 1\,CaO \cdot 8\,MgO \cdot 2\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 5\,B_2O_3 \cdot 1\,Fe_2O_3$	Ohlapian	Jannasch
63	$14\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 8\,H_2O$	$14\,MO = 1.5\,FeO \cdot 1\,CaO \cdot 10\,MgO \cdot 1.5\,Na_2O$ $18\,R_2O_3 = 12.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Orford	Riggs
64	$14\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 8\,H_2O$	$14\,MO = 7\,FeO \cdot 0.5\,CaO \cdot 4.5\,MgO \cdot 1.5\,Na_2O \cdot 0.5\,H_2O;\ 18\,R_2O_3 = 12.5\,Al_2O_3 \cdot 5.5\,B_2O_3$	Haddam	,,
65	$15\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 5\,H_2O$	$15\,MO = 4\,FeO \cdot 0.5\,CaO \cdot 9.5\,MgO \cdot 1\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Kragerö	Rammelsberg
66	$15\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 6\,H_2O$	$15\,MO = 3.5\,FeO \cdot 1.5\,CaO \cdot 8\,MgO \cdot 2\,Na_2O$ $18\,R_2O_3 = 11.5\,Al_2O_3 \cdot 6\,B_2O_3 \cdot 0.5\,Fe_2O_3$	Snarum	Jannasch and Calb
67	$15\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 8\,H_2O$	$15\,MO = 4.5\,FeO \cdot 1.5\,CaO \cdot 8\,MgO \cdot 1\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Baffinsland	Riggs
68	$16\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 4\,H_2O$	$16\,MO = 7.5\,FeO \cdot 0.5\,CaO \cdot 6.5\,MgO \cdot 1.5\,Na_2O$ $18\,R_2O_3 = 12\,Al_2O_3 \cdot 6\,B_2O_3$	Unity	Rammelsberg
69	$20\,MO \cdot 2(9\,R_2O_3 \cdot 12\,SiO_2) \cdot 7\,H_2O$	$20\,MO = 0.5\,FeO \cdot 4\,CaO \cdot 15\,MgO \cdot 0.5\,Na_2O$ $18\,R_2O_3 = 11.5\,Al_2O_3 \cdot 6.5\,B_2O_3$	Hambg.	Riggs

The Fel-

The following analyses of the minerals of the

$$A.\ \bar{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \bar{Si} = 5\,R_2O_3 \cdot 22\,SiO_2,$$

$$B.\ \hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 24\,SiO_2,$$

$$C.\ \bar{Si} \cdot \hat{R} \cdot \bar{Si} \cdot \bar{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 20\,SiO_2,$$

A. Felspars of the type

$$\bar{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \bar{Si} = 5\,R_2O_3 \cdot 22\,SiO_2$$

				Source
1	$3\,MO \cdot 5\,R_2O_3\ \ 22\,SiO_2 \cdot 1\,H_2O$	$3\,MO = 1.5\,Na_2O \cdot 0.5\,CaO \cdot 0.5\,MgO \cdot 0.5\,K_2O$ $5\,R_2O_3 = 4.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	Oligoclase	Cape Wrath
2	$4\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2 \cdot 2\,H_2O$	$4\,MO = 1.5\,Na_2O \cdot 1.75\,CaO \cdot 0.5\,MgO \cdot 0.25\,K_2O$	Andesine	Ale bei Lima
3	$4\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$4\,MO = 1.75\,Na_2O \cdot 1.75\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_2O$	,,	Marmato bei Popayan

	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	Li_2O	Na_2O	K_2O	H_2O	Fl	Total	Loss on Ignition
Theory	36.42	10.60	30.95	—	12.74	—	0.90	—	3.54	—	2.35	—	2.50	—	100.00	—
LI	37.07	9.70	31.86	—	12.55	—	0.51	—	3.49	—	2.04	0.30	2.48	0.31	100.31	—
Theory	37.97	11.05	32.28	—	2.85	—	—	—	10.55	—	2.45	—	2.85	—	100.00	—
XIV	38.51	9.52	32.65	—	2.80	—	0.36	0.16	10.46	—	2.13	0.37	3.04	0.36	100.36	—
Theory	37.14	10.87	31.57	—	7.43	—	—	1.44	7.21	—	1.60	—	2.80	—	100.00	—
XVI	38.00	10.32	31.41	—	7.23	—	—	1.31	7.27	—	1.43	0.28	2.75	—	100.00	—
Theory	37.84	10.09	33.51	—	2.84	—	—	0.74	10.51	—	1.63	—	2.84	—	100.00	—
LIX	38.33	9.86	33.15	—	2.88	—	—	0.77	10.89	—	—	—	2.81	—	100.21	
Theory	37.38	10.80	31.78	--	3.74	—	—	0.73	9.35	—	2.40	—	3.74	—	100.00	—
LIV	36.41	9.65	31.27	—	3.80	1.61	Trace	0.98	9.47	—	2.68	0.21	3.79	—	99.87	3.59
Theory	38.09	11.08	32.38	—	0.95	—	—	1.48	11.64	—	2.46	—	1.92	—	100.00	—
XIII	38.09	11.15	32.90	—	0.66	—	—	1.25	11.79	—	2.37	0.47	2.05	0.64	101.37	—
Theory	36.81	8.93	33.89	—	4.60	—	—	1.43	9.20	—	2.38	—	2.76	—	100.00	—
LXXII	37.70	7.82	34.26	—	4.42	—	—	1.25	9.51	—	2.00	0.43	2.61	—	100.00	—
Theory	35.87	8.70	30.48	3.98	5.38	—	—	1.39	7.97	—	3.09	—	3.14	—	100.00	—
XI	35.69	9.84	30.79	3.65	5.46	0.86	Trace	1.54	8.12	—	2.53	0.27	3.12	—	101.95	—
Theory	36.92	9.85	32.69	—	2.77	—	—	1.44	10.26	—	2.38	—	3.69	—	100.00	—
LX	36.66	10.07	32.84	—	2.50	0.23	Trace	1.35	10.35	Trace	2.42	—	3.78	Trace	100.42	—
Theory	35.51	9.47	31.42	—	12.42	—	—	0.69	4.43	—	2.29	—	3.77	—	100.00	—
LVI	34.95	9.92	31.11	—	11.87	0.57	0.09	0.81	4.45	Trace	2.22	0.24	3.62	—	100.35	2.41
Theory	36.63	10.66	31.14	—	7.33	—	—	0.71	9.67	—	1.57	—	2.29	—	100.00	—
XXIV	37.11	9.29	31.26	—	7.58	—	—	0.80	9.43	—	1.78	0.32	2.43	—	100.00	—
Theory	36.00	10.48	29.32	2.00	6.30	—	—	2.10	8.00	—	3.10	—	2.70	—	100.00	—
XXVI	35.64	9.93	29.41	2.90	6.56	1.10	Trace	1.65	8.00	—	3.03	0.16	2.94	—	101.32	—
Theory	35.85	10.43	30.47	—	8.07	—	—	2.09	7.97	—	1.54	—	3.58	—	100.00	—
LXXI	35.34	10.45	30.49	—	8.22	0.40	Trace	2.32	7.76	Trace	1.76	0.15	3.60	—	100.49	2.88
Theory	35.23	10.29	30.02	—	13.25	—	—	0.69	6.38	—	2.28	—	1.76	—	100.00	—
LXX	26.29	9.04	30.44	—	13.23	—	—	1.02	6.32	—	1.94 + K_2O	—	1.72	—	100.00	—
Theory	35.26	11.12	28.72	—	0.88	—	—	5.49	14.69	—	0.76	—	3.08	0.00	100.00	—
XLVI	35.26	10.45	28.79	—	0.86	0.65	—	5.09	14.58	Trace	0.94	0.18	3.10	0.78	100.37	—

spar Group.

Felspar group conform to the following types :

$$D.\ \overline{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\, R_2O_2 \cdot 22\, SiO_2,$$

$$E.\ \hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\, R_2O_3 \cdot 24\, SiO_2.$$

or the general formula

$$m\, MO \cdot 5\, R_2O_3 \cdot 22\, SiO_2 \cdot n\, H_2O.$$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Heddle	Theory	64.38	23.63	1.95	—	1.37	0.97	2.29	4.53	0.88	100.00
	LXVI	64.54	24.04	2.31	—	1.21	0.77	2.59	4.13	0.84	100.43
Raimondi	Theory	62.98	23.12	1.91	—	4.68	0.95	—	4.43	1.93	100.00
	XCV	63.20	24.00	1.50	—	4.36	0.72	Trace	4.20	1.90	99.88
Deville	Theory	63.32	24.43	—	—	4.69	0.47	1.12	5.20	0.87	100.00
	CIX	63.85	24.05	—	—	5.04	0.38	0.88	5.04	0.76	100.00

				Source
4	$4\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$4\,MO = 2.25\,Na_2O \cdot 1.25\,CaO \cdot 0.5\,K_2O$	Oligoclase	Mer de Glace
5	$4\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$4\,MO = 2.25\,Na_2O \cdot 1.5\,CaO \cdot 0.25\,K_2O$	”	Rispond
6	$4\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$4\,MO = 2.5\,Na_2O \cdot 1\,CaO \cdot 0.5\,K_2O$	”	Vesuvius
7	” ” ”	” ” ” ”	”	Freiberg
8	” ” ”	” ” ” ”	”	Marienberg
9	$4\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	” ” ” ”	”	Arendal
10	$4\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$4\,MO = 2.75\,Na_20 \cdot 0.75\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_2O$	” ”	Danviks Tulb
11	$4\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2$	$4\,MO = 2.75\,Na_20 \cdot 0.75\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_20$; $5\,R_2O_3 = 4.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	”	Röttchen
12	$4\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$4\,MO = 3\,Na_2O \cdot 1\,CaO$	”	Ariége
13	” ” ”	” ” ”	”	Culsagee, N.C.
14	$5\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2$	$5\,MO = 1.75\,Na_2O \cdot 2.5\,CaO \cdot 0.75\,K_2O$ $5\,R_2O_3 = 4.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	”	Neurode
15	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$5\,MO = 2\,Na_2O \cdot 2\,CaO \cdot 0.5\,H_2O \cdot 0.25\,MgO \cdot 0.25\,K_2O$	”	Aberdeen
16	” ” ”	$5\,MO = 2\,Na_2O \cdot 2.5\,CaO \cdot 0.5\,K_2O$	”	Hierro
17	” ” ”	$5\,MO = 2\,Na_2O \cdot 3\,CaO$	”	Campo maior
18	” ” ”	$5\,MO = 2.25\,Na_2O \cdot 2.25\,CaO \quad 0.5\,K_2O$	”	Rosetown, N.J.
19	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	” ” ” ”	”	Pytterlaks
20	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	” ” ” ”	Andesine	Pikruki
21	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$5\,MO = 2.25\,Na_2O \cdot 2.5\,CaO \cdot 0.25\,K_2O$	”	Sardinia
22	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.5\,Na_2O \cdot 1\,CaO \cdot 0.75\,FeO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	Oligoclase	Kjörrestad
23	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.5\,Na_2O \cdot 2\,CaO \cdot 0.25\,K_2O \cdot 0.25\,H_2O$	”	Ditró
24	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$5\,MO = 2.5\,Na_2O \cdot 2\,CaO \cdot 0.5\,K_2O$	”	Comjos, Colorado
25	” ” ”	$5\,MO = 2.5\,Na_2O \cdot 2\,CaO \cdot 0.5\,H_2O$	”	Anna-See
26	” ” ”	$5\,MO = 2.5\,Na_2O \cdot 2.25\,CaO \cdot 0.25\,K_2O$	”	M. Mulatto
27	” ” ”	” ” ” ”	”	Knader
28	” ” ”	$5\,MO = 2.75\,Na_20 \cdot 1.5\,CaO \cdot 0.5\,MgO \cdot 0.25\,H_2O$	”	Chester, Mass.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Theory	63.27	24.44	—	—	3.36	—	2.25	6.68	—	100.00
LVII	63.25	23.92	—	—	3.23	0.32	2.31	6.78	—	99.91
Theory	62.15	21.61	3.77	—	3.95	—	1.11	6.57	0.85	100.00
XLIX	61.85	21.70	3.37	0.20Mn_2O_3	4.13	0.09	1.63	6.95	0.37	100.29
Theory	63.22	24.42	—	—	2.68	—	2.35	7.43	—	100.00
XLIX	62.36	23.38	—	—	2.88	—	2.66	7.42	0.13	98.83
Theory	63.22	24.42	—	—	2.68	—	2.35	7.43	—	100.00
VII	62.97	23.48	0.51	—	2.83	0.24	2.42	7.22	—	99.69
Theory	63.22	24.42	—	—	2.68	—	2.35	7,43	—	100.00
XXXIV	63.20	23.50	0.31	—	2.42	0.25	2.22	7.42	—	99.32
Theory	62.68	24.22	—	—	2.66	—	2.33	7.36	0.85	100.00
LXXVIII	63.53	24.05	—	—	2.60	—	1.86	8.02	0.90	100.96
Theory	63.28	24.45	—	—	2.01	0.96	1.13	8.17	—	100.00
XCII	63.70	23.95	0.50	—	2.05	0.65	1.20	8.11	—	100.16
Theory	63.14	23.18	1.92	—	2.01	0.48	1.12	8.15	—	100.00
XVI	63.16	22.14	2.51	—	2.07	0.65	1.34	8.13	—	100.00
Theory	63.70	24.62	—	—	2.70	—	—	8.98	—	100.00
LIII	62.60	24.60	—	—	3.00	0.20	—	8.90	—	99.40
Theory	63.72	24.61	—	—	2.70	—	—	8.97	—	100.00
CXXXII	64.12	24.20	0.14	—	2.80	—	—	9.28	—	100.54
Theory	61.00	22.40	1.85	—	6.47	—	3.26	5.02	—	100.00
II	61.54	22.36	1.75	—	6.23	—	2.82	4.91	—	99.61
Theory	62.61	24.19	—	—	5.31	0.47	1.11	5.88	0.43	100.00
LXX	62.53	23.52	1.28	—	4.97	0.37	1.32	6.19	0.60	100.78
Theory	61.66	23.82	—	—	6.54	—	2.19	5.79	—	100.00
CLIII	60.99	23.98	0.90	—	6.46	—	2.08	5.44	—	99.85
Theory	62.20	24.04	—	—	7.92	—	—	5.84	—	100.00
LII	61.81	24.45	—	—	8.04	0.34	0.59	6.19	—	101.42
Theory	61.61	23.81	—	—	5.88	—	2.19	6.51	—	100.00
CXXXIV	61.12	23.90	—	—	5.80	—	2.58	6.78	—	100.18
Theory	61.09	23.60	—	—	5.83	—	2.20	6.46	0.82	100.00
CIII	60.90	24.32	—	—	5.78	—	1.87	6.51	0.62	100.00
Theory	61.10	23.60	—	—	5.83	—	2.18	6.46	0.83	100.00
LXXXIII	60.90	24.32	—	—	5.78	—	1.87	6.51	0.62	100.00
Theory	61.88	23.91	—	—	6.56	—	1.11	6.54	—	100.00
LIV	62.65	24.19	—	—	6.28	—	1.24	6.48	—	100.84
Theory	61.50	23.77	—	2.52	2.60	—	1.09	7.22	1.30	100.00
XC	61.80	25.11	—	2.50	2.38	—	0.97	7.18	1.60	101.54
Theory	61.60	23.80	—	—	5.23	—	1.10	7.22	1.05	100.00
XXXVI	61.68	23.95	—	—	5.35	—	1.09	6.99	1.05	100.27
Theory	61.57	23.79	—	—	5.22	—	2.19	7.23	—	100.00
CXXVIII	61.88	24.18	—	—	4.79	—	2.50	6.95	—	100.30
Theory	62.68	24.32	—	—	5.31	—	—	7.36	0.43	100.00
XXXVII	63.05	23.61	—	—	5.28	—	—	7.82	0.24	100.00
Theory	61.84	23.89	—	—	5.91	—	1.10	7.26	—	100.00
XLI	62.84	23.53	—	—	5.50	—	1.15	7.65	—	100.67
Theory	61.84	23.89	—	—	5.91	—	1.10	7.26	—	100.00
LXIV	62.40	23.60	—	—	5.62	—	1.66	7.04	—	100.40
Theory	62.05	23.98	—	—	3.95	0.94	—	8.02	1.06	100.00
CXLIII	62.00	24.40	—	—	3.50	0.70	—	8.07	1.00	99.67

				Source
29	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.5 K_2O \cdot 0.25 H_2O$	Oligoclase	Monnoir, Canada
30	$5\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	,,	Cragie
31	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.5 H_2O \cdot 0.25\,MgO$	,,	Chester, Mass.
32	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.5\,FeO \cdot 0.25\,K_2O$	,,	Kyffhäuser
33	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 1.75\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_2O$	,,	Moland, Arendal
34	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$5\,MO = 2.75\,Na_2O \cdot 1.75\,CaO \cdot 0.25\,FeO \cdot 0.25\,K_2O$	,,	Arendal
35	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 2\,CaO \cdot 0.25\,K_2O$	,,	
36	$5\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	,, ,, ,, ,,	,,	Rhiconich
37	,, ,, ,,	,, ,, ,, ,,	,,	Fredriksvärn
38	,, ,, ,,	$5\,MO = 2.75\,Na_2O \cdot 2.25\,CaO$	,,	Alausi
39	,, ,, ,,	$5\,MO = 3\,Na_2O \cdot 0.5\,CaO \cdot 1.5\,K_2O$	,,	Ditrö
40	,, ,, ,,	$5\,MO = 3\,Na_2O \cdot 2.75\,CaO \cdot 0.25\,K_2O$	,,	Tvedestrand
41	,, ,, ,,	,, ,, ,, ,,	,,	Orenburg
42	,, ,, ,,	$5\,MO = 3\,Na_2O \cdot 2\,CaO$	,,	Perlenhardt
43	,, ,, ,,	,, ,, ,,	,,	Itterby
44	,, ,, ,,	$5\,MO = 3.25\,Na_2O \cdot 1.25\,CaO \cdot 0.5\,MgO$	,,	,,
45	,, ,, ,,	$5\,MO = 3.25\,Na_2O \cdot 1.75\,CaO$	,,	Jestre Kjørrestad b. Bamle
46	,, ,, ,,	,, ,, ,,	,,	Cragie Bukler
47	$6\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2\,Na_2O \cdot 2.25\,CaO \cdot 1\,MgO \cdot 0.75\,K_2O$; $5\,R_2O_3 = 4.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Jamaica Mts. Can.
48	$6\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2$	$6\,MO = 2.25\,Na_2O \cdot 3\,CaO \cdot 0.5\,MgO \cdot 0.25\,K_2O$	,,	Santorino
49	$6\,MO \cdot 5\,R_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2.5\,Na_2O \cdot 1.5\,CaO \cdot 1\,K_2O \cdot 0.5\,MgO \cdot 0.5\,H_2O$; $5\,R_2O_3 = 4.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	,,	Buxburn
50	$6\,MO \cdot 5\,Al_2O_3 \cdot 22\,SiO_2 \cdot 2\,H_2O$	$6\,MO = 2.5\,Na_2O \cdot 2.25\,CaO \cdot 1\,MgO \cdot 0.25\,K_2O$	,,	Gebel Duchan

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Hoffmann	Theory	61.29	23.68	—	—	3.90	—	2.18	7.91	1.04	100.00
	CXLIV	62.05	22.60	—	—	3.96	—	1.80	7.95	0.80	99.91
Heddle	Theory	61.93	22.73	—	—	3.94	—	1.10	8.00	0.42	100.00
	LXXI	61.58	22.00	—	—	4.19	—	1.52	8.27	0.54	99.66
Jackson	Theory	62.05	23.98	—	—	3.95	0.94	—	8.02	1.06	100.00
	CXLIII	62.03	24.40	--	—	3.50	0.70	—	8.07	1.00	99.67
Streng	Theory	61.11	23.61	—	1.66	3.89	—	1.09	7.80	0.84	100.00
	XII	60.94	24.22	—	1.66	3.94	—	0.95	7.65	0.79	100.15
Dirvell	Theory	61.39	23.72	—	—	4.56	0.46	1.09	7.93	0.85	100.00
	LXXXIII	61.84	24.77	—	—	4.20	0.30	0.88	8.14	0.50	100.63
,,	Theory	62.68	24.22	—	—	2.66	—	2.33	7.36	0.85	100.00
	LXXVII	63.53	24.05	—	—	2.60	—	1.86	8.02	0.90	100.96
König	Theory	61.28	23.68	—	—	5.19	—	1.09	7.91	0.85	100.00
	CXIV	60.69	24.24	0.71	—	4.63	—	1.28	7.75	0.85	100.15
Haughton	Theory	61.81	23.87	—	—	5.24	—	1.10	7.98	—	100.00
	LXXV	61.88	24.80	—	—	4.93	—	0.98	8.12	—	100.71
Pisani	Theory	61.81	23.87	—	—	5.24	—	1.10	7.98	—	100.00
	LXXXVII	62.25	24.80	0.25	—	4.90	—	0.80	7.80	0.20	101.00
Siemiradzki	Theory	62.08	23.98	—	—	5.92	—	—	8.02	—	100.00
	CXXIV	61.58	25.30	—	—	6.08	—	—	8.14	—	101.10
Fellner	Theory	59.43	22.97	—	—	1.96	—	6.35	8.37	1.62	100.00
	XXXV	60.28	22.40	—	—	1.17	0.09	6.37	8.44	1.61	100.36
Scheerer	Theory	61.75	23.86	—	—	4.58	—	1.10	8.71	—	100.00
	LXXXVI	61.30	23.77	0.36	—	4.78	—	1.29	8.50	—	100.00
G. v. Rath	Theory	61.75	23.86	—	—	4.58	—	1.10	8.71	—	100.00
	CXVII	60.34	24.39	0.18	—	5.56	—	0.73	8.44	0.33	99.97
,,	Theory	62.04	23.96	—	—	5.26	—	—	8.74	—	100.00
	XV	62.18	23.52	—	—	5.33	—	—	8.97	—	100.00
Jannetaz	Theory	62.04	23.96	—	—	5.26	—	—	8.74	—	100.00
	XCV	63.19	23.52	—	—	4.81	—	—	9.01	—	100.53
Berzelius	Theory	62.23	24.04	—	—	3.29	0.94	—	9.50	—	100.00
	XCIII	61.55	23.80	—	—	3.18	0.80	0.38	9.67	—	99.38
G. v. Rath	Theory	61.98	23.95	—	—	4.61	—	—	9.46	—	100.00
	LXXXIX	61.91	23.68	—	—	4.45	—	—	9.64	—	100.00
Haughton	Theory	61.98	23.95	—	—	4.61	—	—	9.46	—	100.00
	LXXII	62.00	23.20	—	—	4.71	—	—	9.20	—	100.00
Hunt	Theory	59.26	20.16	3.59	—	5.66	1.80	3.16	5.57	0.80	100.00
	CXLVII	58.60	21.10	2.88	—	5.40	1.84	3.08	5.51	0.80	99.21
Fouqué	Theory	60.52	23.39	—	—	7.71	0.92	1.07	6.39	—	100.00
	LI	59.70	23.20	0.40	—	7.90	1.00	0.80	6.60	—	99.60
Heddle	Theory	59.34	21.78	1.80	—	3.77	0.90	4.23	6.97	1.21	100.00
	LXIX	59.53	21.05	1.81	—	3.63	0.88	4.73	7.23	1.88	100.74
Delesse	Theory	59.71	23.07	—	—	5.70	1.81	1.06	7.01	1.64	100.00
	CXLVIII	58.92	22.49	0.75	0.60MnO	5.53	1.87	0.93	6.93	1.64	99.60

B. Felspars of the type

$\hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si} = 5\,R_2O_3 \cdot 24\,SiO_2$

				Source
51	$4\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$4\,MO = 2.25\,Na_2O \cdot 0.5\,CaO \cdot 0.75\,K_2O \cdot 0.5\,MgO$	Oligoclase	Lessines
52	$4\,MO \cdot 5\,R_2O_3 \cdot 24\,SiO_2$	$4\,MO = 2.75\,Na_2O \cdot 0.75\,CaO \cdot 0.5\,K_2O$	,,	Old Meldrum
53	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 2.25\,Na_2O\ \ 2.5\,CaO \cdot 0.25\,K_2O$	,,	Furth
54	,, ,, ,,	$5\,MO = 2.5\,Na_2O \cdot 1\,CaO \cdot 1\,K_2O \cdot 0.5\,MgO$	,,	Hartenberg
55	,, ,, ,,	$5\,MO = 2.5\,Na_2O \cdot 1.5\,CaO \cdot 0.75\,H_2O \cdot 0.25\,K_2O$	,,	Visembach
56	,, ,, ,,	$5\,MO = 2.5\,Na_2O \cdot 1.5\,CaO \cdot 1\,K_2O$	,,	Pierrepont, N.S.
57	,, ,, ,,	$5\,MO = 2.75\,Na_2O \cdot 0.75\,CaO \cdot 1\,K_2O \cdot 0.5\,MgO$ $5\,R_2O_3 = 4.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Ajatskaja
58	$5\,MO \cdot 5\,R_2O_3\ \ 24\,SiO_2$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	,,	Coyle, Aberdeen
59	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 3\,Na_2O \cdot 0.75\,CaO \cdot 1\,K_2O \cdot 0.25\,MgO$	,,	Pico de Teneriffe
60	,, ,, ,,	,, ,, ,, ,, ,,	,,	,,
61	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 3\,Na_2O \cdot 1\,CaO \cdot 0.5\,K_2O \cdot 0.5\,H_2O$	,,	Badenweiler
62	$5\,MO \cdot 5\,Al_2O_3 . 24\,SiO_2$	$5\,MO = 3\,Na_2O \cdot 1.5\,CaO \cdot 0.5\,K_2O$	,,	Wittichen
63	,, ,, ,,	,, ,, ,, ,,	,,	Gaggenau
64	,, ,, ,,	$5\,MO = 3.25\,Na_2O \cdot 1\,MgO \cdot 0.75\,K_2O$	,,	Laacher See
65	,, ,, ,,	$5\,MO = 3.25\,Na_2O\ \ 1.25\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_2O$	,,	Coromandel
66	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 3.25\,Na_2O \cdot 1.5\,CaO \cdot 0.25\,K_2O$	,,	Veltlin
67	,, ,, ,,	,, ,, ,, ,,	,,	Niedermendig
68	,, ,, ,,	,, ,, ,, ,,	,,	Itterby
69	,, ,, ,,	,, ,, ,, ,,	,,	(Granite)
70	,, ,, ,,	,, ,, ,, ,,	,,	Lairg
71	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 3.5\,Na_2O \cdot 0.5\,CaO \cdot 0.75\,K_2O \cdot 0.25\,MgO$	,,	Pico de Teneriffe
72	,, ,, ,,	$5\,MO = 3.5\,Na_2O \cdot 0.75\,CaO \cdot 0.5\,K_2O \cdot 0.25\,MgO$	,,	Arendal
73	,, ,, ,,	$5\,MO = 3.5\,Na_2O \cdot 0.75\,CaO \cdot 0.75\,K_2O$	,,	Boden
74	,, ,, ,,	$5\,MO = 3.5\,Na_2O \cdot 1.25\,CaO \cdot 0.25\,K_2O$	,,	Danbury, Conn.

or the general formula

$m\,MO \cdot 5\,R_2O_3 \cdot 24\,SiO_2 \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Delesse	Theory	64.66	22.91	—	—	1.28	0.90	3.17	6.27	0.81	100.00
	LXI	63.70	22.64	0.53	—	1.44	1.20	2.81	6.15	1.22	99.69
Heddle	Theory	64.75	21.78	1.80	—	1.89	—	2.11	7.67	—	100.00
	LXVIII	64.67	22.18	1.44	—	1.89	0.02	1.54	7.64	0.15	99.53
v. Gümbel	Theory	63.92	22.64	—	—	6.21	—	1.04	6.19	—	100.00
	XXXI	64.40	23.07	—	0.27	5.61	—	0.96	5.85	—	100.16
G. v. Rath	Theory	63.30	22.42	—	—	2.46	0.88	4.13	6.81	—	100.00
	XIV	63.50	21.81	0.66	—	2.32	0.95	3.65	6.84	—	99.81
Delesse	Theory	64.69	22.91	—	—	3.77	—	1.06	6.96	0.61	100.00
	XXIII	63.88	22.27	—	—	3.45	—	1.21	6.66	0.70	98.68
Penfield and Sperry	Theory	63.08	22.34	—	—	3.68	—	4.12	6.78	—	100.00
	CXL	63.76	22.67	0.41	—	3.05	—	3.60	6.89	0.40	100.78
Francis	Theory	62.45	19.92	3.48	—	1.82	0.87	4.07	7.39	—	100.00
	CXI	61.06	19.68	4.11	—	2.16	1.05	3.91	7.55	—	99.52
Heddle	Theory	63.95	21.54	1.78	—	3.73	—	1.04	7.57	0.39	100.00
	LXVII	63.54	21.45	1.86	—	3.88	0.23	1.07	7.64	0.44	100.11
Delesse	Theory	63.11	22.35	—	—	1.84	0.44	4.11	8.15	—	100.00
	CXLIX	62.97	22.29	—	—	2.06	0.54	3.69	8.45	—	100.00
”	Theory	63.11	22.35	—	—	1.84	0.44	4.11	8.15	—	100.00
	CL	62.54	22.49	—	—	2.18	0.41	4.54	7.84	—	100.00
Wollemann	Theory	63.55	22.51	—	—	2.47	—	2.07	8.21	1.19	100.00
	XXIV	63.22	22.95	—	—	2.50	—	1.93	8.12	1.36	100.35
Hebenstreit	Theory	63.52	22.50	—	—	3.71	—	2.07	8.20	—	100.00
	XXV	62.90	22.23	—	—	4.45	—	2.09	8.48	—	100.15
Seneca	Theory	63.52	22.50	—	—	3.71	—	2.07	8.20	—	100.00
	XXVIII	63.63	22.52	—	—	3.85	0.44	2.29	8.39	—	100.12
Fouqué	Theory	63.66	22.55	—	—	—	1.77	3.11	8.91	—	100.00
	XIX	63.50	22.10	—	—	0.30	1.80	3.40	8.90	—	100.00
Pisani	Theory	63.86	22.63	—	—	3.10	0.44	1.04	8.93	—	100.00
	CXXI	64.00	23.50	—	—	2.72	0.60	0.77	9.00	0.16	100.75
G. v. Rath	Theory	63.74	22.58	—	—	3.72	—	1.04	8.92	—	100.00
	XLVI	64.58	23.08	—	—	3.49	—	0.62	8.98	—	100.75
”	Theory	63.74	22.58	—	—	3.72	—	1.04	8.92	—	100.00
	XVII	63.06	23.27	—	—	4.16	—	0.62	8.93	—	100.04
Lemberg	Theory	63.74	22.58	—	—	3.72	—	1.04	8.92	—	100.00
	XCIX	63.38	22.98	—	—	3.62	—	0.55	9.10	0.37	100.00
G. v. Rath	Theory	63.74	22.58	—	—	3.72	—	1.04	8.92	—	100.00
	CXIII	63.83	22.58	--	—	3.42	—	1.02	8.86	—	100.15
Heddle	Theory	63.74	22.58	—	—	3.72	—	1.04	8.92	—	100.00
	LXXIII	62.81	22.92	0.16	—	4.25	0.08	0.84	8.53	0.29	99.88
Delesse	Theory	63.28	22.43	—	—	1.23	0.44	3.00	9.54	—	100.00
	CLI	63.81	21.98	—	—	1.10	0.66	2.99	9.46	—	100.00
Hagen	Theory	63.56	22.51	—	—	1.85	0.44	2.07	9.57	—	100.00
	LXXVI	63.51	23.09	—	—	2.44	0.77	2.19	9.37	—	101.37
Kerndt	Theory	63.17	22.38	—	—	1.84	—	3.09	9.52	—	100.00
	IV	61.66	22.56	0.35	0.40 MnO	2.02	0.10	3.08	9.43	—	100.00
Smith and Brush	Theory	63.71	22.56	—	—	3.09	—	1.04	9.60	—	100.00
	CXLI	63.76	22.56	—	—	3.09	—	0.55	9.72	0.26	99.94

				Source
75	$5\,MO \cdot 5\,Al_2O_o \cdot 24\,SiO_2$	$5\,MO = 3.5\,Na_2O \cdot 1.25\,CaO\ \ 0.25\,K_2O$	Oligoclase	Telemarken
76	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 3.5\,Na_2O \cdot 1.5\,CaO$	,,	Smin
77	$5\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 4\,Na_2O \cdot 0.75\,CaO \cdot 0.25\,K_2O$	,,	Turin
78	$6\,MO \cdot 5\,Al_2O_3 \cdot 24\,SiO_2$	$6\,MO = 2.75\,Na_2O \cdot 2.25\,CaO \cdot 0.5\,FeO \cdot 0.25\,MgO \cdot 0.25\,K_2O$	,,	Kyffhäuser
79	,, ,, ,,	$6\,MO = 3.25\,Na_2O \cdot 2.75\,CaO$	,,	Alagnon
80	,, ,, ,,	$6\,MO = 4\,Na_2O \cdot 2\,CaO$	,,	Pargas

C. Felspars of the type $\bar{Si} \cdot \hat{R} \cdot \bar{Si} \cdot \bar{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 20\,SiO_2$

				Source
81	$5\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 1.75\,Na_2O \cdot 2.75\,CaO \cdot 0.25\,MgO \cdot 0.25\,H_2O$	Andesine	St. Raphael in Esterelgebirge bei Tréjus
82	$5\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 4\,H_2O$	$5\,MO = 2\,Na_2O \cdot 2.75\,CaO \cdot 0.25\,K_2O$	,,	Dubniok
83	$5\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$5\,MO = 2\,Na_2O \cdot 3\,CaO$	,,	Adamelle-Gebirge
84	$5\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$5\,MO = 2.25\,Na_2O \cdot 2.5\,CaO \cdot 0.25\,MgO$; $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Descaberado Chico
85	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 4.75\,CaO \cdot 1.25\,FeO$	Labradorite	Silicite, Antrim
86	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 3\,H_2O$	$6\,MO = 1.25\,Na_2O \cdot 3.25\,CaO \cdot 0.75\,K_2O \cdot 0.5\,MgO \cdot 0.25\,H_2O$	,,	Lakonien
87	$6\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$6\,MO = 1.25\,Na_2O \cdot 4\,CaO \cdot 0.5\,MgO \cdot 0.25\,K_2O$; $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Nicolosi
88	,, ,, ,,	$6\,MO = 1.25\,Na_2O \cdot 4.25\,CaO \cdot 0.5\,H_2O$; $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	,,	Kiew
89	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$6\,MO = 1.25\,Na_2O \cdot 4.25\,CaO \cdot 0.5\,K_2O$	Andesine	Tunguragua
90	$6\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$6\,MO = 1.25\,Na_2O \cdot 4.5\,CaO \cdot 0.25\,MgO$; $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	Labradorite	Lhama
91	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 2\,H_2O$	$6\,MO = 1.5\,Na_2O \cdot 3.5\,CaO \cdot 0.75\,FeO \cdot 0.25\,K_2O$	Andesine	Recsk b. Erlau
92	$6\,MO \cdot 6\,Al_2O_3 \cdot \cdot 20\,SiO_2$	$6\,MO = 1.5\,Na_2O \cdot 4.5\,CaO$	,,	Muretto Pass
93	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 2\,H_2O$	$6\,MO = 1.75\,Na_2O \cdot 3\,CaO \cdot 0.75\,K_2O \cdot 0.25\,MgO \cdot 0.25\,H_2O$	,,	Odenwald
94	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 3\,H_2O$	$6\,MO = 1.75\,Na_2O \cdot 3.25\,CaO \cdot 0.75\,H_2O \cdot 0.25\,K_2O$	,,	Oberstein
95	$6\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$6\,MO = 1.75\,Na_2O \cdot 3.5\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$; $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	,,	Château Richer, Canada
96	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$6\,MO = 1.75\,Na_2O \cdot 4\,CaO \cdot 0.25\,K_2O$	,,	Le Prese
97	,, ,, ,,	,, ,, ,, ,,	,,	Hohe Wald, Odenwald

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Pisani	Theory	63.71	22.56	—	—	3.09	—	1.04	9.60	—	100.00
	LXXXVIII	65.30	23.00	—	—	2.42	—	0.70	9.65	0.20	101.27
C. v. Hauer	Theory	63.46	22.49	—	—	3.70	—	—	9.56	0.79	100.00
	XXXIII	63.16	23.16	—	—	3.00	—	0.17	9.72	0.79	100.00
Rocholl	Theory	63.62	22.53	—	—	1.85	—	1.04	10.96	—	100.00
	XLVII	62.52	22.40	—	—	2.29	—	1.19	10.78	—	99.18
Streng	Theory	60.76	21.52	—	—	5.32	0.42	0.99	7.19	2.28	100.00
	XI	60.01	21.66	—	—	5.15	0.68	1.37	7.06	2.59	100.08
Fouqué	Theory	62.46	22.12	—	—	6.68	—	—	8.74	—	100.00
	LIX	62.40	22.80	—	—	7.00	—	0.50	8.40	—	101.10
Bonsdorff	Theory	62.34	22.08	—	—	4.84	—	—	10.74	—	100.00
	CI	62.03	21.34	1.00	—	4.86	—	—	10.77	—	100.00

or the general formula
$m\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2 \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Deville	Theory	56.96	29.04	—	—	7.31	0.47	—	5.15	1.07	100.00
	LVII	57.01	28.05	—	—	7.53	0.39	0.12	5.47	1.43	100.00
K. v. Hauer	Theory	54.91	28.00	—	—	7.05	—	1.08	5.67	—	100.00
	XXXVII	55.61	28.64	—	—	7.00	—	1.55	5.59	—	101.63
Val. San Valentino	Theory	57.04	29.09	—	—	7.98	—	—	5.89	—	100.00
	XLIX	56.79	28.48	—	—	8.56	—	0.34	6.10	0.24	100.51
Domeyko	Theory	56.33	26.33	3.75	—	6.57	0.47	—	6.55	—	100.00
	XCII	55.30	26.50	4.30	—	6.20	0.60	—	6.70	—	99.60
Thomson	Theory	54.90	28.00	—	4.12	12.17	—	—	—	0.81	100.00
	LXXVI	54.80	28.40	—	4.00	12.40	—	—	—	0.60	100.20
Delesse	Theory	54.04	27.56	—	—	8.19	0.90	3.18	3.49	2.64	100.00
	CXXI	53.20	27.31	1.03	—	8.02	1.01	3.40	3.52	2.51	100.00
S. v. Walters-hausen	Theory	54.90	25.66	3.66	—	10.25	0.91	1.08	3.54	—	100.00
	LXXI	55.83	25.31	3.63	—	10.49	0.74	0.83	3.52	—	100.35
Segeth	Theory	55.79	27.27	1.86	—	11.07	—	—	3.60	0.41	100.00
	CXVIII	55.49	26.83	1.60	—	10.93	0.15	0.36	3.96	0.51	99.83
Siemiradzki	Theory	55.19	28.14	—	—	10.95	—	2.16	3.56	—	100.00
	CIII	54.89	28.97	—	—	10.28	—	1.72	3.61	—	99.47
Koto	Theory	55.41	27.07	1.85	—	11.63	0.46	—	3.58	—	100.00
	CXXVIII	55.97	27.60	1.68	—	11.88	0.66	0.08	3.83	—	101.70
K. v. Hauer	Theory	54.19	27.63	—	2.43	8.85	—	1.06	4.20	1.64	100.00
	XXXVI	53.99	26.78	—	2.22	9.09	0.30	0.82	4.21	1.90	99.31
Mattirolo	Theory	55.63	28.37	—	—	11.68	—	—	4.32	—	100.00
	LII	55.53	28.38	—	—	11.72	—	—	4.13	0.24	100.00
Behr	Theory	54.32	27.70	—	—	7.60	0.45	3.19	4.91	1.83	100.00
	XIX	54.70	27.49	0.55	—	7.64	0.42	2.76	4.64	1.65	99.85
Delesse	Theory	54.71	27.90	—	—	8.30	—	1.07	4.94	3.08	100.00
	XI	53.89	27.66	0.97	—	8.28	—	1.28	4.92	3.00	100.00
Hunt	Theory	55.47	27.11	1.85	—	9.06	—	1.08	5.01	0.42	100.00
	CXXII	55.80	26.90	1.53	—	9.01	0.27	0.86	4.77	0.45	99.59
G. v. Rath	Theory	55.36	28.23	—	—	10.33	—	1.08	5.00	—	100.00
	LI	55.15	29.15	—	—	9.90	—	0.80	5.23	—	100.23
Swiatkowski	Theory	55.36	28.23	—	—	10.33	—	1.08	5.00	—	100.00
	XVIII	55.24	29.02	—	—	9.91	0.19	1.31	5.13	—	100.80

				Source
98	$6\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$6\,MO = 1.75\,Na_2O \cdot 4\,CaO \cdot 0.25\,K_2O$	Labradorite	Labrador
99	„ „ „	„ „ „ „	„	„
100	„ „ „	„ „ „ „	„	Campsie
101	„ „ „	„ „ „ „	„	Schriesheim
102	„ „ „	$6\,MO = 1.75\,Na_2O \cdot 4\,CaO \cdot 0.25\,H_2O$	„	Suligata
103	„ „ „	„ „ „ „	„	Nagyag
104	„ „ „	„ „ „ „	„	Piatra Poienitia
105	„ „ „	„ „ „ „	„	Palma
106	„ „ „	„ „ „ „	„	Rotundo
107	„ „ „	„ „ „ „	„	Kisbánya
108	„ „ „	$6\,MO = 1.75\,Na_2O \cdot 4.25\,CaO$	Andesine	Pomasque
109	„ „ „	$6\,MO = 2\,Na_2O \cdot 3.75\,CaO \cdot 0.25\,K_2O$	„	Langlangchi
110	$6\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$6\,MO = 2\,Na_2O \cdot 3.75\,CaO \cdot 0.25\,MgO$ $6\,R_2O_3 = 5.25\,Al_2O_3 \cdot 0.75\,Fe_2O_3$	Labradorite	Baumholder
111	$7\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$7\,MO = 0.5\,Na_2O \cdot 3.75\,CaO \cdot 1.75\,K_2O \cdot 0.75\,H_2O \cdot 0.25\,MgO$	„	Labrador
112	$7\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$7\,MO = 1.5\,Na_2O \cdot 3.75\,CaO \cdot 1\,MgO \cdot 0.5\,H_2O$ $0.25\,MnO$; $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	„	Val del Bove
113	$7\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2 \cdot 1\,H_2O$	$7\,MO = 1.5\,Na_2O \cdot 4\,CaO \cdot 1\,MgO \cdot 0.25\,MnO \cdot 0.25\,H_2O$; $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	„	Etna
114	$7\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2 \cdot 1\,H_2O$	$7\,MO = 1.5\,Na_2O \cdot 4.75\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_2O \cdot 0.25\,H_2O$	„	Mascali
115	$7\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 1\,H_2O$	$7\,MO = 1.5\,Na_2O \cdot 4.75\,CaO \cdot 0.5\,MgO \cdot 0.25\,K_2O$	„	Montarville
116	$7\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 2\,H_2O$	$7\,MO = 1.75\,Na_2O \cdot 3\,CaO \cdot 0.75\,H_2O \cdot 0.75\,FeO \cdot 0.5\,MgO \cdot 0.25\,K_2O$	Andesine	Ilfeld
117	$7\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$7\,MO = 1.75\,Na_2O \cdot 4.5\,CaO \cdot 0.5\,FeO \cdot 0.25\,K_2O$	Labradorite	Labrador
118	„ „ „	$7\,MO = 2\,Na_2O \cdot 4.25\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	„	Monte Amiata
119	„ „ „	$7\,MO = 2\,Na_2O \cdot 5\,CaO$	„	Geschiebe bei Berlin
120	$7\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2 \cdot 1\,H_2O$	$7\,MO = 2.25\,Na_2O \cdot 3.75\,CaO \cdot 0.5\,H_2O \cdot 0.5\,K_2O$	Andesine	Illowa
121	$7\,MO \cdot 6\,Al_2O_3 \cdot 20\,SiO_2$	$7\,MO = 2.25\,Na_2O \cdot 3.75\,CaO \cdot 0.75\,H_2O \cdot 0.25\,K_2O$	„	Rawdon
122	$8\,MO \cdot 6\,R_2O_3 \cdot 20\,SiO_2$	$8\,MO = 2.75\,Na_2O \cdot 5.25\,CaO$	„	Los Pescadores

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Tschermak	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	CLII	56.00	27.50	0.70	—	10.10	0.10	0.40	5.00	—	99.80
Klement	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	CLIII	56.10	27.33	1.38	—	10.33	—	0.36	5.17	—	100.75
Lehunt	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	LXXXIX	54.67	27.89	0.31	0.18 MnO	10.60	—	0.49	5.05	—	99.19
	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	XXIX	55.24	29.02	—	—	9.91	0.19	1.31	5.13	—	100.80
Delter	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	XLI	55.22	28.93	—	—	9.95	—	0.28	5.01	—	99.39
,,	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	XLIII	54.76	29.09	—	—	10.10	—	0.62	5.00	—	99.57
,,	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	XLII	55.95	28.41	—	—	9.85	—	0.43	5.05	—	99.67
G. v. Rath	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	CLXXI	55.64	28.89	—	—	10.92	—	0.71	5.09	—	101.25
Delter	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	XLIV	55.93	28.15	—	—	9.84	—	0.69	5.27	—	99.88
Delesse	Theory	55.35	28.23	—	—	10.33	—	1.08	5.01	—	100.00
	XLVIII	56.05	28.11	—	—	10.10	—	0.99	4.65	—	99.90
G. v. Rath	Theory	55.60	28.35	—	—	11.03	—	—	5.02	—	100.00
	CV	55.86	28.10	—	—	10.95	—	—	5.09	—	100.00
,,	Theory	55.31	28.21	—	—	9.68	—	1.08	5.72	—	100.00
	XCVII	55.64	28.19	1.02	—	9.79	0.19	2.63	5.48	—	100.44
E. E. Schmid	Theory	54.56	24.35	5.46	—	9.55	0.44	—	5.64	—	100.00
	XXI	53.41	24.88	4.89	—	9.42	0.44	—	5.62	—	98.66
S. v. Walters-hausen	Theory	53.55	27.31	—	—	9.37	0.45	7.34	1.38	0.60	100.00
	CLI	53.75	27.06	0.99	—	9.58	0.47	7.53	1.25	0.62	101.25
Abich	Theory	54.63	26.71	1.82	0.81 MnO	9.56	1.82	—	4.23	0.42	100.00
	LXVII	53.48	26.46	1.60	0.89 MnO	9.47	1.74	0.22	4.10	0.42	98.40
Ricciardi	Theory	53.51	26.15	1.78	0·79 MnO	9.99	1.78	1.05	4.15	0.80	100.00
	LXXII	53.33	26.13	2.87	0.59 MnO	10.34	1.64	0.51	3.97	0.84	100.22
S. v. Walters-hausen	Theory	53.19	24.87	3.55	—	11.79	0.44	1.04	4.12	1.00	100.00
	LXX	53.56	25.82	3.41	—	11.68	0.52	0.58	4.00	0.95	100.42
Hunt	Theory	53.75	27.42	—	—	11.92	0.89	1.05	4.16	0.81	100.00
	CXLV	53.10	26.80	1.35	—	11.48	0.72	0.71	4.24	0.60	99.00
Streng	Theory	53.68	27.38	—	2.42	7.51	0.89	1.05	4.85	2.22	100.00
	III	53.11	27.27	—	2.53	7.47	0.91	1.08	5.09	2.38	99.84
Jannasch	Theory	53.76	27.42	—	1.61	11.29	—	1.06	4.86	—	100.00
	CLV	54.09	27.82	—	1.50	11.20	0.05	0.43	4.76	0.19	100.04
Williams	Theory	54.38	27.74	—	—	10.79	—	1.06	5.62	0.41	100.00
	LVIII	55.04	28.09	—	—	10.65	—	1.26	5.61	0.50	101.15
Dulk	Theory	54.15	27.62	—	—	12.64	—	—	5.59	—	100.00
	VII	54.66	27.87	—	—	12.01	—	—	5.46	—	100.00
K. v. Hauer	Theory	53.69	27.37	—	—	9.39	—	2.10	6.24	1.21	100.00
	XL	54.53	27.37	—	—	9.62	—	1.81	5.98	1.21	100.52
Hunt	Theory	54.58	27.84	—	—	9.55	—	1.07	6.35	0.61	100.00
	CXXVI	54.45	28.05	0.45	—	9.68	—	1.06	6.25	0.55	100.49
Domeyko	Theory	52.38	25.60	1.75	—	12.83	—	—	7.44	—	100.00
	XCI	50.50	25.40	2.10	—	12.25	0.35	—	7.30	0.04	97.94

D. Felspars of the type

$$\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si} = 6\,R_2O_3 \cdot 22\,SiO_2$$

				Source
123	$4\,MO \cdot 6\,R_2O_3 \cdot 22\,SiO_2 \cdot 3\,H_2O$	$4\,MO = 2.5\,Na_2O \cdot 0.5\,CaO \cdot 0.5\,MgO \cdot 0.5K_2O$; $6R_2O_3 = 5.75Al_2O_3 \cdot 0.25\,Fe_2O_3$	Andesine	Mairus (Ardennes)
124	$5\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2 \cdot 2\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 2.25\,CaO$	,,	Tilasinvuori
125	$6\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2$	$6\,MO = 1.75\,Na_2O \cdot 3.25\,CaO \cdot 0.75\,H_2O \cdot 0.25\,MgO$	,,	St. Raphael in Esterelgeb.
126	,, ,, ,,	$6\,MO = 2\,Na_2O \cdot 3.25\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	,,	Château Richer, Can.
127	,, ,, ,,	$6\,MO = 2\,Na_2O \cdot 3.25\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	,,	Lachute
128	$6\,MO \cdot 6\,Al_2O_3\ \ 22\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2\,Na_2O \cdot 3.5\,CaO \cdot 0.5\,K_2O$	,,	St. Raphael in Esterelgeb.
129	$6\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2$	$6\,MO = 2\,Na_2O \cdot 3.75\,CaO \cdot 0.25\,K_2O$	,,	St. Joachim
130	,, ,, ,,	$6\,MO = 2\,Na_2O \cdot 4\,CaO$	Labradorite	Ojamo
131	,, ,, ,,	$6\,MO = 2.25\,Na_2O \cdot 3.5\,CaO \cdot 0.25\,K_2O$	Andesine	St. Raphael in Esterelgeb.
132	,, ,, ,,	,, ,, ,, ,,	Labradorite	Labrador
133	,, ,, ,,	,, ,, ,, ,,	,,	Krakatan
134	$6\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	,, ,, ,, ,,	Andesine	Château Richer, Can.
135	$6\,MO \cdot 6\,Al_2O \cdot 22\,SiO_2 \cdot 2\,H_2O$	,, ,, ,, ,,	,,	Sanford, Me.
136	$6\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2$	$6\,MO = 2.25\,Na_2O \cdot 3.75\,CaO$	,,	Tunguragua
137	,, ,, ,,	$6\,MO = 2.5\,Na_2O \cdot 3.25\,CaO \cdot 0.25\,MgO$	,,	Niedermendig
138	,, ,, ,,	$6\,MO = 2.5\,Na_2O \cdot 3.5\,CaO$	,,	Guaqua Pichincha
139	,, ,, ,,	,, ,, ,,	,,	Trifail
140	,, ,, ,,	,, ,, ,,	Labradorite	Ojamo
141	$7\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2 \cdot 2\,H_2O$	$7\,MO = 1.75\,Na_2O \cdot 4\,CaO \cdot 0.75\,H_2O \cdot 0.5\,K_2O$	Andesine	Gratlue
142	$7\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2 \cdot 1\,H_2O$	$7MO = 1.75\,Na_2O \cdot 4.25\,CaO \cdot 0.75\,H_2O \cdot 0.25\,K_2O$	Labradorite	Monte Amiata
143	$7\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2$	$7\,MO = 1.75\,Na_2O \cdot 5\,CaO \cdot 0.25\,MgO$	,,	Verespatek
144	,, ,, ,,	$7\,MO = 2\,Na_2O \cdot 3\,CaO \cdot 1\,FeO \cdot 0.75\,K_2O \cdot 0.25\,MgO$	Andesine	Luccivna, N. Tatra
145	$7\,MO \cdot 6\,Al_2O_3 \cdot 22\,SiO_2 \cdot 5\,H_2O$	$7\,MO = 2\,Na_2O \cdot 3\,CaO \cdot 1\,FeO \cdot 0.75\,K_2O \cdot 0.25\,MgO$	,,	,,
146	$9\,MO \cdot 6\,Al_2O_8 \cdot 22\,SiO_2 \cdot 3\,H_2O$	$9\,MO = 2\,Na_2O \cdot 6.75\,CaO \cdot 0.25\,MgO$	,,	St. Raphael in Esterelgeb

or the general formula

$m\,MO \cdot 6\,R_2O_3 \cdot 22\,SiO_2 \cdot n\,H_2O$.

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Klement	Theory	58.65	26.06	1.78	—	1.24	0.89	2.09	6.89	2.40	100.00
	LXVIII	59.78	26.69	2.05	—	1.35	0.58	1.69	7.29	2.25	101.68
Wilk	Theory	58.37	27.06	—	—	6.16	—	—	6.82	1.59	100.00
	LXXVIII	58.39	26.68	—	—	5.63	—	—	7.69	1.61	100.00
Deville	Theory	58.78	27.25	—	—	8.10	0.44	—	4.83	0.60	100.00
	LVI	59.07	26.67	—	—	7.96	0.58	Trace	4.95	0.77	100.00
Hunt	Theory	58.13	26.95	—	—	8.02	—	1.04	5.46	0.40	100.00
	CXXI	58.50	25.80	1.00	—	8.06	0.20	1.16	5.45	0.40	100.57
"	Theory	58.13	26.95	—	—	8.02	—	1.04	5.46	0.40	100.00
	CXXV	58.15	26.09	0.50	—	7.78	0.16	1.21	5.55	0.45	99.89
Rammelsberg	Theory	56.98	26.41	—	—	8.46	—	2.03	5.35	0.77	100.00
	LV	58.32	26.52	—	—	8.18	0.11	2.36	5.27	0.60	101.36
Hunt	Theory	57.66	26.72	—	—	9.17	—	1.03	5.42	—	100.00
	CXXIV	57.55	27.10	0.20	—	8.73	—	0.79	5.38	—	99.75
Bonsdorff and Laurell	Theory	57.90	26.85	—	—	9.82	—	—	5.43	—	100.00
	CXIV	57.69	26.00	0.67	—	9.87	—	—	5.50	—	99.73
Rammelsberg	Theory	57.62	26.71	—	—	8.55	—	1.03	6.09	—	100.00
	LIX	58.03	26.64	—	—	8.07	—	0.97	6.16	0.30	99.87
Lemberg	Theory	57.62	26.71	—	—	8.55	—	1.03	6.09	—	100.00
	CLVII	57.36	27.01	—	—	8.55	—	0.65	6.03	—	100.00
"	Theory	57.62	26.71	—	—	8.55	—	1.03	6.09	—	100.00
	CXXV	58.29	27.19	—	—	8.27	—	1.22	5.82	—	100.79
Hunt	Theory	57.17	26.51	—	—	8.49	—	1.02	6.04	0.77	100.00
	CXXIII	57.20	26.40	0.40	—	8.34	—	0.84	5.83	0.65	99.60
Payne	Theory	56.72	26.30	—	—	8.42	—	1.01	6.00	1.55	100.00
	CXVI	56.65	25.56	0.22	—	8.25	—	1.34	6.18	1.58	99.78
G. v. Rath	Theory	57.86	26.82	—	—	9.20	—	—	6.12	—	100.00
	CII	57.80	26.75	—	—	9.05	—	—	6.40	—	100.00
Laspeyres	Theory	57.92	26.86	—	—	7.98	0.44	—	6.80	—	100.00
	X	57.29	26.78	—	—	8.01	0.28	—	6.84	Trace	99.20
G. v. Rath	Theory	57.82	26.81	—	—	8.58	—	—	6.79	—	100.00
	C	58.15	26.10	—	—	9.05	—	—	6.70	—	100.00
Maly	Theory	57.82	26.81	—	—	8.58	—	—	6.79	—	100.00
	XLVII	57.53	26.62	—	—	8.48	0.23	0.39	6.90	—	100.15
Williams	Theory	57.82	26.82	—	—	8.58	—	—	6.78	—	100.00
	CXV	57.75	26.15	0.60	—	8.48	—	—	6.25	—	99.23
Heddle	Theory	55.91	25.92	—	—	9.49	—	1.99	4.60	2.09	100.00
	LXXII	56.30	25.71	0.97	—	9.35	—	1.49	4.72	1.82	100.36
Williams	Theory	56.56	26.23	—	—	10.20	—	1.01	4.65	1.35	100.00
	LVI	55.68	26.66	—	—	10.30	—	1.43	4.70	1.23	100.00
Sipöcz	Theory	56.64	26.26	—	—	12.02	0.42	—	4.66	—	100.00
	XXXVII	55.21	25.56	1.00	—	11.76	0.53	—	4.37	—	101.43
Höfer	Theory	55.54	25.75	—	3.03	7.07	0.42	2.97	5.22	—	100.00
	XXIX	56.04	25.55	—	3.12	7.19	0.59	2.59	4.92	—	100.00
"	Theory	53.51	24.81	—	2.92	6.81	0.41	2.86	5.03	3.65	100.00
	XXVIII	53.26	24.28	—	2.96	6.83	0.56	2.47	4.68	3.98	99.02
Deville	Theory	52.84	24.51	—	—	15.13	0.40	—	4.96	2.16	100.00
	LVIII	52.42	24.78	—	—	15.02	0.51	0.14	5.10	2.03	100.00

E. Felspars of the type

$\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si} = 6\,R_2O_3 \cdot 24\,SiO_2$

				Source
147	$4\,MO \cdot 6\,R_2O_3 \cdot 24\,SiO_2 \cdot 6\,H_2O$	$4\,MO = 2\,Na_2O \cdot 0.75\,CaO\ 0.75\,K_2O \cdot 0.5\,MgO$; $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	Oligoclase	Helsingfors
148	$4\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$4\,MO = 2\,Na_2O \cdot 1.75\,CaO \cdot 0.25\,K_2O$	,,	Tokowaja
149	,, ,,	$4\,MO = 2.25\,Na_2O \cdot 1.5\,CaO \cdot 0.25\,K_2O$	,,	Bakersville, N.C.
150	$5\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 2\,Na_2O \cdot 2\,CaO \cdot 1\,K_2O$	Andesine	Horberig
151	$5\,MO \cdot 6\,R_2O_3 \cdot 24\,SiO_2 \cdot 5\,H_2O$	$5\,MO = 5\,Na_2O \cdot 2.25\,CaO \cdot 0.75\,K_2O$ $6\,R_2O_3 = 5.5\,Al_2O_3 \cdot 0.5\,Fe_2O_3$	,,	Milltown
152	$5\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 2\,H_2O$	$5\,MO = 2.25\,Na_2O \cdot 2\,CaO \cdot 0.75\,K_2O$	Oligoclase	Durrmorsbach
153	$5\,MO \cdot 6\,R_2O_3 \cdot 24\,SiO_2$	$5\,MO = 2.5\,Na_2O \cdot 2\,CaO \cdot 0.5\,K_2O$ $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	,,	Ardara
154	$5\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$5\,MO = 2.5\,Na_2O \cdot 2.5\,CaO$	Andesine	Milltown Csicso-Berg
155	$5\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 2\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.75\,K_2O$	Oligoclase	Allemont
156	$5\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 2\,H_2O$	$5\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 0.5\,MgO \cdot 0.25\,K_2O$	,,	Bourg d'Oísans
157	$5\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$5\,MO = 3\,Na_2O \cdot 2\,CaO$	,,	Carter-MineN.C.
158	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 1.5\,Na_2O \cdot 4\,CaO \cdot 0.25\,K_2O \cdot 0.25\,FeO$	Andesine	Kyffhäuser
159	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$6\,MO = 2\,Na_2O \cdot 3.25\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	,,	Château Richer, Canada
160	,, ,, ,,	$6\,MO = 2.25\,Na_2O \cdot 3.25\,CaO \cdot 0.25\,MgO \cdot 0.25\,K_2O$	,,	Frauenberg bei Schlüchtern
161	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2.5\,Na_2O \cdot 2.25\,CaO \cdot 0.75\,MgO \cdot 0.5\,K_2O$	,,	La Bresse
162	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2.5\,Na_2O \cdot 2.5\,CaO \cdot 0.5\,K_2O \cdot 0.5\,H_2O$	,,	Cullakenee, Clay Co., N.C.
163	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2.5\,Na_2O \cdot 2.5\,CaO \cdot 0.75\,H_2O \cdot 0.25\,K_2O$	,,	Faymont
164	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2.5\,Na_2O \cdot 2.5\,CaO \cdot 0.75\,H_2O \cdot 0.25\,K_2O$	,,	Sebesvár
165	$6\,MO \cdot 6\,R_2O_3 \cdot 24\,SiO_2$	$6\,MO = 2.5\,Na_2O \cdot 2.5\,CaO \cdot 0.75\,MgO \cdot 0.25\,K_2O$; $6\,R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25\,Fe_2O_3$	,,	Marmato bei Popayan
166	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$6\,MO = 2.5\,Na_2O \cdot 2.75\,CaO \cdot 0.5\,H_2O \cdot 0.25\,K_2O$	,,	Coromandel
167	,, ,, ,,	$6\,MO = 2.5\,Na_2O \cdot 3\,CaO \cdot 0.25\,MgO \cdot 0.25\,H_2O$	,,	Budenmais
168	,, ,, ,,	$6\,MO = 2.5\,Na_2O \cdot 3.5\,CaO$	,,	Pululagua
169	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 2\,H_2O$	$6\,MO = 2.75\,Na_2O \cdot 1.5\,CaO \cdot 1\,K_2O \cdot 0.5\,H_2O \cdot 0.25\,MgO$	Oligoclase	Unionville, Pa.
170	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 2.75\,Na_2O \cdot 2\,CaO \cdot 0.5\,K_2O \cdot 0.5\,H_2O \cdot 0.25\,MgO$	Andesine	Servance

or the general formula

$m\,MO \cdot 6\,R_2O_3 \cdot 24\,SiO_2 \cdot n\,H_2O.$

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Lemberg	Theory	58.88	22.94	3.27	—	1.72	0.82	2.88	5.07	4.42	100.00
	CVI	58.30	23.15	4.09	—	1.65	0.59	2.52	5.26	4.44	100.00
Jewreinow	Theory	62.68	26.64	—	—	4.26	—	1.02	5.40	—	100.00
	CXV	60.63	26.35	0.40	—	4.15	0.25	1.17	5.60	—	98.55
Clarke	Theory	62.64	26.61	—	—	3.65	—	1.02	6.07	—	100.00
	CXXIX	62.92	25.32	—	—	4.03	—	0.96	6.18	0.25	99.66
Knop	Theory	60.45	25.69	—	—	4.71	—	3.94	5.21	—	100.00
	XVII	60.01	25.49	—	—	4.71	—	4.06	5.77	—	100.04
Heddle	Theory	57.81	22.51	3.21	—	5.06	—	2.83	4.97	3.61	100.00
	LXIX	58.38	22.50	2.12	0.15 MnO	5.34	—	3.20	5.21	3.41	100.31
Haushofer	Theory	59.75	25.40	—	—	4.65	—	2.92	5.79	1.49	100.00
	XXIX	59.30	25.75	—	—	4.79	—	2.78	5.63	1.29	99.54
Haughton	Theory	60.49	24.64	1.68	—	4.71	—	1.97	6.51	—	100.00
	LXIII	59.28	22.96	1.94	0.32 MnO	4.65	0.21	2.38	6.48	—	98.22
Koch	Theory	60.89	25.88	—	—	5.92	—	—	6.55	0.76	100.00
	XLVI	61.62	25.47	—	—	5.72	—	—	6.31	0.88	100.00
Lory	Theory	59.68	25.36	—	—	3.48	—	2.92	7.07	1.49	100.00
	LIV	59.40	24.20	0.60	—	3.70	—	3.80	7.00	1.50	99.80
,,	Theory	60.35	25.65	—	—	3.52	0.84	0.98	7.15	1.51	100.00
	LV	59.90	25.10	—	—	3.70	0.70	1.20	7.40	1.70	99.70
Keller	Theory	61.29	26.04	—	—	4.76	—	—	7.91	—	100.00
	CXXXI	62.32	25.19	—	—	5.01	—	0.25	8.02	—	100 79
Streng	Theory	59.30	25.20	—	0.74	9.23	—	0.96	3.83	0.74	100.00
	V	59.16	25.97	—	1.04	9.23	0.03	0.47	3.91	0.68	100.49
Hunt	Theory	60.24	25.60	—	—	7.61	—	0.98	5.19	0.38	100.00
	CXVII	59.55	25.62	0.75	—	7.73	Trace	0.96	5.09	0.45	100.15
Wedel	Theory	59.82	25.42	—	—	7.65	0.43	0.98	5.79	—	100.00
	VII	59.19	25.77	0.34 (Fe_2O_3+FeO)		7.27	0.27	0.80	5.88	0.37 TiO_2	99.89
Delesse	Theory	59.31	25.21	—	—	5.19	1.24	1.93	6.38	0.74	100.00
	XVI	58.55	25.26	0.30	—	5.03	1.30	1.50	6.44	0.91	99.29
Chatard	Theory	59.48	25.28	—	—	5.78	—	1.94	6.40	1.12	100.00
	CXV	58.41	25.93	0.38	—	5.82	0.18	2.10	6.42	0.93	100.20
Delesse	Theory	59.96	25.48	—	—	5.83	—	0.97	6.45	1.31	100.00
	XV	59.38	25.57	—	—	6.50	—	7.03		1.25	100.00
K. v. Haue	Theory	59.96	25.48	—	—	5.83	—	0.97	6.45	1.31	100.00
	XLII	59.50	25.48	—	—	5.82	—	1.43	6.43	1.35	100.07
Abich	Theory	59.63	24.28	1.66	—	5.80	1.24	0.97	6.42	—	100.00
	CVI	59.60	24.28	1.58	—	5.77	1.08	1.08	6.53	—	99.92
Dirvell	Theory	60.16	25.57	—	—	6.43	—	0.98	6.48	0.38	100.00
	LXXXIV	61.32	25.30	—	—	6.50	—	1.19	6.30	0.50	101.11
Foullon	Theory	59.79	25.41	—	—	6.99	0.41	0.97	6.43	—	100.00
	XXVI	59.22	25.08	0.96	—	7.08	0.28	0.54	6.79	—	100.78
G. v. Rath	Theory	59.93	25.47	—	—	8.15	—	—	6.45	—	100.00
	XCIX	59.39	26.08	—	—	8 20	—	0.22	6.74	—	100.63
Chatard	Theory	58.65	24.92	—	—	3.42	0.41	3.83	6.94	1.83	100.00
	CXXXVII	59.35	24.16	0.61	—	3.08	0.34	3.78	7.22	1.96	100.50
Delesse	Theory	59.54	25.31	—	—	4.63	0.41	1.94	7.05	1.12	100.00
	XIII	58.92	25.05	—	—	4.64	0.41	2.06	7.20	1.27	99.50

				Source
171	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$6\,MO = 2.75\,Na_2O \cdot 2.25\,CaO \cdot 0.75\,K_2O \cdot 0.25\,MgO$	Oligoclase	Beloceil
172	,, ,, ,,	$6\,MO = 2.75\,Na_2O \cdot 3\,CaO \cdot 0.25\,K_2O$	Andesine	Heubach
173	,, , ,,	,, ,, ,, ,,	,,	(Château Richer, Canada) Toluca
174	,, ,, ,,	$6\,MO = 3\,Na_2O \cdot 1.75\,CaO \cdot 0.75\,H_2O \cdot 0.25\,MgO \cdot 0.25\,K_2O$	Oligoclase	Norway
175	$6\,MO \cdot 6\,Al_2O_3\ \ 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 3\,Na_2O \cdot 1.75\,CaO \cdot 0.75\,K_2O \cdot 0.25\,MgO \cdot 0.25\,H_2O$	Andesine	Coravillers
176	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$6\,MO = 3\,Na_2O \cdot 2\,CaO \cdot 0.5\,K_2O \cdot 0.5H_2O$	Oligoclase	Altai
177	$6\,MO\ \ 6\,R_2O_3 \cdot 24\,SiO_2 \cdot 3\,H_2O$	$6\,MO = 3\,Na_2O \cdot 2.5\,CaO \cdot 0.25\,MgO \cdot 0.25Na_2O$: $6R_2O_3 = 5.75\,Al_2O_3 \cdot 0.25Fe_2O_3$	Andesine	Frankenstein
178	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$6\,MO = 3\,Na_2O \cdot 2.75\,CaO \cdot 0.25\,K_2O$	,,	Marmato bei Popayan
179	,, ,, ,,	$6\,MO = 3\,Na_2O \cdot 3\,CaO$	,,	Mojanda
180	,, ,, ,,	$6\,MO = 3.75\,Na_2O \cdot 2.25\,CaO$	,,	Bodenmais
181	$6\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 3\,H_2O$	$6\,MO = 4\,Na_2O \cdot 2\,CaO$	,,	,,
182	$7\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 3\,H_2O$	$7\,MO = 2.5\,Na_2O \cdot 3.25\,CaO \cdot 0.75\,H_2O \cdot 0.5\,K_2O$	,,	Szaszka
183	$7\,MO \cdot 6\,R_2O_3 \cdot 24\,SiO_2 \cdot 1\,H_2O$	$7\,MO = 2.5\,Na_2O \cdot 3.5\,CaO \cdot 0.5\,K_2O \cdot 0.5H_2O$; $6R_2O_3 = 5.75Al_2O_3 \cdot 0.25Fe_2O_3$	,,	Château Richer, Canada
184	$7\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 2\,H_2O$	$7\,MO = 2.75\,Na_2O \cdot 3.5\,CaO \cdot 0.75\,K_2O$	,,	Delnabo Glen Gairu
185	$7\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2 \cdot 2\,H_2O$	$7\,MO = 3\,Na_2O \cdot 3.25\,CaO \cdot 0.5\,K_2O \cdot 0.25\,H_2O$	,,	Nagy Sebes
186	$7\,MO \cdot 6\,Al_2O_3 \cdot 24\,SiO_2$	$7\,MO = 3\,Na_2O \cdot 3.25\,CaO \cdot 0.5\,K_2O \cdot 0.25\,MgO$	,,	Marmato bei Popayan
187	,, ,, ,,	$7\,MO = 3.5\,Na_2O \cdot 3\,CaO \cdot 0.5\,MgO$	Oligoclase	Baumgarten

Analyst		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	Total
Hoffmann	Theory	59.28	25.19	—	—	5.19	0.42	7.02	7.02	—	100.00
	CXLV	58.30	24.72	—	—	5.42	0.91	2.74	6.72	0.50	99.32
Petersen	Theory	59.66	25.36	—	—	6.95	—	0.97	7.06	—	100.00
	XX	58.77	25.30	0.31	(Fe_2O_3+FeO)	6.90	0.18	0.60	6.67	0.28 TiO_2	99.01
G. v. Rath	Theory	59.66	25.36	—	—	6.95	—	0.97	7.06	—	100.00
	CXIII	59.79	25.43	—	—	7.41	—	0.64	7.24	—	100.51
Dirvell	Theory	60.42	25.68	—	—	4.11	0.42	0.99	7.81	0.57	100.00
	LXXV	61.14	25.10	—	—	4.39	0.50	1.17	7.66	0.80	100.76
Delesse	Theory	59.04	25.09	—	—	4.02	0.41	2.89	7.63	0.92	100.00
	XIV	58.91	24.59	0.99	—	4.01	0.39	2.54	7.59	0.98	100.00
Christschoff	Theory	59.16	25.15	—	—	4.60	—	1.93	8.05	1.11	100.00
	CXVIII	58.89	25.38	—	—	4.69	—	1.35	7.65	1.17	99.25
Schmidt	Theory	58.10	23.70	1.61	0.75 NiO	5.66	0.40	—	7.52	2.18	100.00
	I	58.93	23.50	1.27	0.39 NiO	5.67	0.56	0.50	7.42	2.21	100.00
Rammelsberg	Theory	59.62	25.23	—	—	6.38	—	0.97	7.70	—	100.00
	CVII	60.26	25.01	—	—	6.87	0.14	0.84	7.74	—	100.86
G. v. Rath	Theory	59.85	25.44	—	—	6.98	—	—	7.73	—	100.00
	XCVIII	60.48	25.35	—	—	7.25	—	0.08	7.28	—	100.44
A. Ohl	Theory	59.74	25.39	—	—	5.23	—	—	9.64	—	100.00
	XXIV	60.35	26.13	—	—	5.14	—	—	9.32	—	100.94
H. Schulze	Theory	59 26	25.17	—	—	4.62	—	—	10.21	0.74	100.00
	XXIII	58.36	25.72	—	—	4.76	—	—	10.18	0.51	99.63
Sommaruga	Theory	57.52	24.46	—	—	7.26	—	1.88	6.19	2.69	100.00
	XXXIX	56.51	24.94	—	—	7.08	—	1.28	6.37	2.55	98.73
Franke	Theory	57.80	23.53	1.61	—	7.87	—	1.89	6.22	1.08	100.00
	CXX	58.38	23.86	1.18	—	7.83	—	1.68	6.05	1.03	100.11
Heddle	Theory	57.03	24.23	—	—	7.77	—	2.79	6.75	1.43	100.00
	LXXI	56.96	23.81	0.94	—	7.98	0.09	2.56	6.85	1.62	100.81
K. v. Hauer	Theory	57.42	24.41	—	—	7.26	—	1.87	7.42	1.62	100.00
	XLI	57.20	25.12	—	—	6.96	—	1.87	7.28	1.68	100.11
Jacobson	Theory	58.13	24.71	—	—	7.35	0.40	1.90	7.51	—	100.00
	CVIII	60.14	25.39	0.87	—	7.93	0.53	1.66	7.99	—	104.51
Varrentrapp	Theory	58.61	24.92	—	—	6.83	0.81	—	8.83	—	100.00
	III	58.41	25.23	—	—	6.54	0.41	—	9.39	—	99.98

A. Formulæ from a Series of Analyses of Allophanes.

I.	0.5 CaO	6 Al_2O_3	6 SiO_2	32 H_2O
Calcd.	1.77	38.77	22.96	36.50
Found	1.92	37.73	23.53	36.86

II.	0.5 CaO	6 Al_2O_3	6 SiO_2	38 H_2O
Calcd.	1.66	36.29	21.48	40.57
Found	1.96	35.20	21.39	40.86

III.	0.75 CaO	6 Al_2O_3	6 SiO_2	32 H_2O
Calcd.	2.63	38.44	22.75	36.17
Found	2.83	38.76	22.65	35.14

IV.	0.25 CaO	6 Al_2O_3	5 SiO_2	32 H_2O
Calcd.	0.93	40.69	20.07	38.30
Found	0.70	41.00	19.80	37.70

V.	0.75 CaO	6 Al_2O_3	6 SiO_2	42 H_2O
Calcd.	2.37	34.53	20.45	42.65
Found	2.23	31.34	20.50	42.91

B. Formulæ from Clay Analyses in C. Bischof's Book.

(a) $\hat{Si} \cdot \hat{R} \cdot \hat{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
2.87	0.28	0.23	0.44	26.73	61.46	8.26	—	100.27	0.48	3.10	12.00	5.37	78	Mähren, Briesen
0.27	0.54	0.13	3.06	24.52	62.73	8.88	—	100.13	0.21	2.98	12.00	5.65	66	Göppersdorf, Silesian Prussia
3.15	0.52	0.10	1.12	26.27	61.35	7.53	—	100.04	0.56	3.10	12.00	4.90	68	Tschirne, Silesian Prussia
1.45	0.54	0.51	0.83	26.93	62.66	7.38	—	100.30	0.43	3.09	12.00	4.69	68	,, ,, ,,

(b) $\bar{Si} \cdot \hat{R} \cdot \bar{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
2.11	Trace	0.15	3.42	26.94	58.02	9.39	—	100.03	0.26	2.95	10.00	5.39	71	Lothain b. Meißen, Saxony.
2.11	0.47	0.40	1.86	28.55	58.35	8.59	—	100.33	0.42	2.99	10.00	4.91	87	Sergejewka, Russia.
1.24	0.55	0.61	2.03	27.98	56.59	9.92	1.08 C.	100.15	0.39	3.03	10.00	5.83	86	Borowitschi, Russia.
2.99	0.37	0.26	1.35	28.31	59.01	7.93	—	100.22	0.46	2.91	10.00	4.48	53	Neitzert i. Bendorf, Prussia.
1.26	0.28	0.34	1.71	28.31	59.78	8.27	0.052	100.02	0.26	2.89	10.00	4.61	83	Sonkolyo, Hungary.
0.88	0.33	0.36	1.04	29.26	57.97	9.98	0.09 S.	99.91	0.25	3.03	10.00	5.74	86	Borowitschi, Russia.
1.26	0.24	0.13	0.97	28.88	58.63	10.50	—	100.01	0.22	2.90	10.00	5.97	71	Löthain b. Meißen, Saxony.
0.75	0.34	0.28	1.17	29.15	58.26	10.00	—	100.05	0.22	3.02	10.00	5.77	71	,, ,, ,,
0.73	0.15	0.46	0.89	29.57	57.71	10.68	—	100.19	0.21	3.06	10.00	6.17	75	Michelob, Bohemia.
0.54	Trace	0.07	1.16	28.68	59.58	9.87	—	99.90	0.07	2.91	10.00	5.52	71	Löthain b. Meißen, Saxony.
0.60	0.13	0.12	0.76	29.99	58.04	10.59	0.08 S.	100.31	0.12	3.08	10.00	6.08	71	,, ,, ,,

(c) $\hat{R}\left\langle\begin{matrix}\hat{Si}\\ \hat{Si}\\ \hat{Si}\end{matrix}\right.$

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
1.02	—	—	1.77	18.93	72.05	6.13	0.10 S.	100.00	0.14	2.98	18.00	5.12	59	Großalmerode, Prussia.

(d) $\hat{R}\left\langle\begin{matrix}\bar{Si}\\ \bar{Si}\\ \bar{Si}\end{matrix}\right.$

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
0.55	0.33	0.18	0.63	23.65	65.69	9.11	0.09 S.	100.23	0.23	3.22	15.00	6.93	71	Löthain b. Meißen, Saxony.
2.19	0.16	0.24	1.67	23.08	65.35	7.46	—	100.15	0.43	3.25	15.00	5.70	67	Ober-Horka, Prussia.
0.85	0.08	0.07	1.40	23.02	67.48	7.34	—	100.24	0.16	3.12	15.00	5.44	50	Dillenburg, Prussia.
0.80	0.09	0.43	0.71	23.61	66.58	7.90	—	100.12	0.25	3.18	15.00	5.93	77	Blansko, Mähren.

(e) $\hat{Si} \cdot \hat{R} \cdot \hat{R} \cdot \hat{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
0.57	38.46	0.02	0.29	24.51	28.12	6.38	1.87	100.22	24.62	6.19	12.00	9.08	57	Westerland, Prussia.
1.32	0.07	0.06	2.74	37.09	47.22	10.79	—	100.19	0.26	5.81	12.00	6.09	74	Eger, Austria.
3.00	0.11	0.04	0.95	37.95	46.97	10.02	—	99.04	0.54	5.79	12.00	8.53	52	Ebernhalm, Prussia.
2.00	0.18	0.12	1.65	38.17	44.90	12.85	—	99.93	0.63	6.16	12.00	11.45	74	Eger, Austria.
0.51	0.21	0.32	0.41	37.73	46.21	14.22	0.39	100.02	0.35	5.81	12.00	12.31	57	Westerland, Prussia.

(f) $\hat{Si} \cdot \bar{R} \cdot \bar{R} \cdot \hat{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
4.28	0.95	0.62	1.24	32.72	48.92	11.49	—	100.23	1.18	4.83	12.00	9.39	78	Briesen, Mähren.
1.64	15.79	0.13	0.33	29.64	42.53	7.52	2.61	100.91	7.72	4.92	12.00	7.07	57	Westerland, Prussia.
2.73	0.49	0.32	2.94	33.63	49.43	10.59	—	100.13	0.83	5.09	12.00	8.54	44	Grünstadt,Bavaria.
3.21	0.41	0.48	1.79	33.09	50.72	10.49	—	100.19	0.75	4.77	12.00	8.27	44	" "
2.30	0.79	0.56	2.22	24.76	49.60	9.96	—	100.19	0.78	4.91	12.00	8.03	44	" "
2.65	0.69	0.34	1.73	33.57	50.39	10.85	—	100.22	0.73	4.86	12.00	8.61	44	" "
3.86	0.63	0.43	1.27	35.39	49.76	8.83	—	100.17	0.93	5.12	12.00	7.09	54	Höhr b.Grenzhausen,Prus.
3.14	0.67	0.40	2.24	33.91	48.92	10.92	—	100.10	0.84	5.09	12.00	8.84	44	Grünstadt, Bavaria.
3.38	0.55	0.33	2.07	34.61	48.85	10.18	—	99.97	0.82	5.19	12.00	8.33	44	" "
2.73	0.45	0.34	2.00	33.76	50.12	10.63	—	100.03	0.67	4.94	12.00	8.48	44	" "
1.51	0.73	0.76	1.66	34.95	49.48	11.04	0.26 S.	100.39	0.69	5.13	12.00	8.92	58	Großalmerode, Prussia.
1.81	0.44	0.48	1.90	34.09	49.49	11.63	0.036S.	99.87	0.56	5.03	12.00	9.40	46	Gem.Mechenhart,Bavaria.
1.59	14.56	0.02	0.08	30.33	41.14	10.02	2.10	99.84	7.20	5.17	12.00	9.63	57	Westerland,Prussia.
2.66	0.21	0.40	2.00	33.71	49.86	11.13	—	99.97	0.58	4.95	12.00	8.92	44	Grünstadt,Bavaria.
3.79	0.15	0.23	1.16	33.71	47.76	13.26	—	100.06	0.72	5.09	12.00	11.10	80	Briesen, Mähren.
1.33	0.76	0.51	1.84	35.60	49.66	10.04	—	99.74	0.67	5.23	12.00	8.09	44	Grünstadt, Bavaria.
2.78	0.18	0.33	1.06	34.41	50.03	11.46	—	100.25	0.57	4.95	12.00	9.16	76	Wildstein, Bohemia.
1.30	0.28	0.05	1.89	33.64	48.23	14.63	0.15 S.	100.78	0.32	5.10	12.00	12.13	83	Göttweig, South Austria.
1.41	0.23	0.34	1.00	34.89	51.17	10.85	—	99.89	0.38	5.02	12.00	8.48	77	Blansko, Mähren.
1.04	0.29	0.21	0.60	35.71	50.00	11.98	—	99.94	0.31	5.08	12.00	9.56	77	" "

(g) $\hat{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \hat{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
2.41	0.68	0.42	1.00	30.11	56.04	9.44	—	100.10	0.96	5.81	18.00	10.10	68	Tschirne, Prussia.
0.38	0.25	0.15	0.70	31.71	55.47	11.40	—	100.06	0.25	6.13	18.00	12.33	72	Löthain b. Meißen, Saxony.

(h) $\bar{Si} \cdot \hat{R} \cdot \hat{Si} \cdot \hat{R} \cdot \bar{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O	R_2O_3	SiO_2	H_2O	Page	Source
1.67	0.57	0.43	1.78	31.58	53.14	10.69	0.04	99.98	0.71	5.79	16.00	10.73	46	Gem.Mechenhart,Bavaria.
3.01	0.39	0.42	2.00	32.54	50.91	10.42	0.10	99.79	0.87	6.25	16.00	10.94	54	Höhr b.Grenzhausen,Prus.
0.60	0.31	1.31	1.20	30.65	50.40	15.65	—	100.12	0.71	5.87	16.00	16.56	87	Novgorod, Russia.
2.92	0.28	0.31	1.23	33.56	51.96	9.62	—	99.84	1.41	6.22	16.00	9.87	76	Wildstein, Bohemia.
1.37	0.45	0.49	1.50	33.11	54.66	8.73	—	99.69	0.61	5.93	16.00	8.61	46	Klingenberg a.M. Bavaria.
1.37	0.45	0.49	1.50	34.08	53.09	8.71	0.11 S	100.00	0.62	6.20	16.00	8.75	61	Ahrtal, Prussia.
0.61	0.23	0.13	0.65	33.61	52.11	12.80	—	100.14	0.24	6.14	16.00	13.10	71	Löthain b.Meißen,Saxony.

(i) $\hat{Si} \cdot \bar{R} \cdot \hat{Si} \cdot \bar{R} \cdot \hat{Si}$.

K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	H_2O	Na_2O	Total	R_2O_3	R_2O_3	SiO_2	H_2O	Page	Source
1.40	0.34	0.10	0.72	27.40	60.15	8.00	0.21 FeO	98.32	0.45	4.91	18.00	7.97	84	Namur, Belgium.
1.99	0.30	0.21	0.79	28.30	60.21	8.59	—	100.39	0.57	5.06	18.00	8.59	49	Odenwald,Hessen-Darmstadt.

C. Formulæ from Clay Analyses in C. Bischof's Book.

I	0.5 CaO	2.75 Al_2O_3	0.25 Fe_2O_3	15 SiO_2	5.5 H_2O	
Calcd.	2.06	20.72	2.95	66.95	7.32	Source : Tiegelerdberg (Bavaria).
Found.	2.25	20.97	2.25	66.70	7.53	Analyst : H. Kaul, *l.* c. p. 47.

II.	0.25 K_2O	19.75 H_2O	0.25 Fe_2O_3	9.75 Al_2O_3	24 SiO_2	Source : Winkelhaid (Bavaria).
Calcd.	0.82	12.42	1.40	34.73	50.62	Analyst : H. Kaul, *l.* c. p. 47.
Found.	0.95	12.11	1.38	35.72	49.80	0.15 CaO 0.18 Na_2O 0.09 S

III.	0.25 MgO	0.25 K_2O	0.25 Fe_2O_3	5.75 Al_2O_3	16 SiO_2	15.5 H_2O	Source : Wolfshöhe (Bavaria)
Calcd.	0.52	1.23	2.09	30.77	50.73	14.64	Analyst : H. Kaul, *l.* c. p. 47.
Found.	0.59	1.09	1.56	31.26	49.61	14.43	0.26 CaO 0.29 Na_2O

IV.	0.5CaO	15.5H_2O	0.25Fe_2O_3	5.75Al_2O_3	16SiO_2	Source : Passau (South Bavaria).
Calcd.	1.47	14.68	2.10	30.86	50.88	Kerl, Handb. d. ges. Tonw. 1879, 505, *l. c.* 48.
Found.	1.63	14.23	1.05	31.11	51.02	0.80 H_2O

VI.	0.25 Fe_2O_3	5.75 Al_2O_3	16 SiO_2	Source : Stabbarp (Sweden).
Calcd.	2.51	36.81	60.68	Analyst : Cronquist, Stockholm (*l.* c. p. 41).
Found.	1.70	36.10	60.80	0·5 CaO 0.5 K_2O 0.2 MgO

VIII.	0.5 K_2O	8.5 H_2O	5 Al_2O_3	16 SiO_2	Source : Finsing b. Deggendorf.
Calcd.	2.80	9.12	30.41	57.66	Analyst : C. Bischof, *l.* c. p. 43.
Found.	3.17	8.67	29.47	57.45	0.75 Fe_2O_3 0.76 (MgO+CaO)

IX.	0.25 Fe_2O_3	5.75 Al_2O_3	15 SiO_2	0.5 K_2O	9.5 H_2O	Source : Grünstadt (Rheinpfalz).
Calcd.	2.28	33.50	51.77	2.68	9.77	Analyst : C. Bischof.
Found.	1.79	33.09	50.70	3.21	10.49	0.41 MgO 0.18 CaO

X.	6 Al_2O_3	12 SiO_2	Source : Altwasser, Grube Morgen- und Abendstern.
Calcd.	45.78	54.22	Analyst : C. Bischof (*l.* c. p. 36).
Found.	45.07	54.03	0.15 MgO 0.25 Fe_2O_3 0.54 K_2O

XI.	0.25K_2O	0.25CaO	0.25Fe_2O_3	5.75Al_2O_3	16 SiO_2	
Calcd.	1.44	0.86	2.45	35.96	59.29	Source : Passau (Bavaria).
Found.	0.90	1.20	1.90	36.40	59.60	Analyst : Cronquist, Stockholm, *l.*c. p. 48.

XII.	0.25 K_2O	9.75 H_2O	0.5 Fe_2O_3	5.5 Al_2O_3	16 SiO_2	Source : Schwarzwald (Oberpfalz).
Calcd.	1.30	9.71	4.42	31.05	53.51	Analyst : C. Bischof (*l.* c. p. 48).
Found.	1.33	10.50	3.41	30.69	53.10	0.32 MgO 0.26 CaO

XIII.	12 H_2O	5.75 Al_2O_3	0.25 Fe_2O_3	18 SiO_2	Source : Klingenberg a. M.
Calcd.	11.19	30.39	2.07	56.34	Analyst : unknown (*l.* c. p. 46).
Found.	11.14	30.47	1.51	56.44	0.30 MgO 0.79 CaO 0.30 K_2O

XIV.	0.5 Fe_2O_3	5.5 Al_2O_3	16 SiO_2	12 H_2O	Source : Klingenberg a. M.
Calcd.	4.38	30.76	53.01	11.81	Analyst : Vohl, 1875.
Found.	3.54	31.61	52.32	11.81	0.48 CaO

XV.	0.5 Fe_2O_3	4.5 Al_2O_3	12 SiO_2	10 H_2O	Source : Klingenberg a. M.
Calcd.	5.54	31.79	50.20	12.47	
Found.	4.22	32.00	51.05	12.14	0.46 CaO

XVI.	0.25 MgO	0.25 CaO	0.25 K_2O	9.25 H_2O	0.25 Fe_2O_3	5.75 Al_2O_3	16 SiO_2
Calcd.	0.55	0.77	1.30	9.21	2.21	32.45	53.50
Found.	0.50	0.50	1.37	9.12	1.50	33.11	54.06

Source : Klingenberg. Analyst : C. Bischof, 1887.

D. Behaviour of Clays, dried at 100° C., towards Sulphuric Acid, according to C. Bischof.

Number	%									Molecular Ratios				Separated SiO_2 in		Al_2O_3 : SiO_2 in Solution
	H_2O	K_2O	MgO	FeO	CaO	Al_2O_3	Fe_2O_3	SiO_2	Total	H_2O	R_2O	R_2O_3	SiO_2	%	Mol.	
1	9.40	1.15	0.20	—	0.04	29.96	0.45	58.80	100	9.11	0.31	5.17	17	25.66	7.42	5 : 10
2	8.41	2.09	0.28	—	0.56	30.34	0.67	57.65	100	7.83	0.65	5.05	16	21.35	5.8	5 : 10
3	7.44	2.31	0.25	—	0.06	25.73	0.60	63.61	100	4.70	0.36	2.91	12	36.68	6.91	6 : 10
4	10.03	3.22	0.45	0.44	0.28	27.99	0.44	56.98	100	10.04	1.01	5.00	17	21.28	6.34	5 : 11
5	7.27	1.21	0.64	0.40	0.08	22.30	0.50	67.60	100	5.41	0.46	2.97	15	41.87	9.29	6 : 10
6	8.14	1.42	0.34	0.21	0.10	27.87	0.73	61.19	100	8.03	0.49	4.93	18	26.91	7.91	5 : 10
7	15.13	1.61	0.85	—	0.42	36.32	1.00	44.67	100	11.60	0.75	5.94	12	4.67	1.26	6 : 11

Ultramarines.

Formulæ from a series of Ultramarine Analyses.

No.									Total	Reference
		Si_{12}	Al_{12}	Na_{12}	S_4	O_{60}			Total	
1.	Theory.	16.60	16.01	13.64	6.32	47.43	—	—	100.00	
	Found.	16.45	14.36	14.45	6.00	48.74	—	—	100.00	Rickmann, Dingl. Journ. *232*, 164.
		Si_{12}	Al_{12}	$Na_{13.5}$	$K_{0.5}$	S_4	O_{57}			
2.	Theory.	16.55	15.96	15.30	0.96	6.31	44.92	—	100.00	
	Found.	16.87	15.39	15.66	0.72	5.69	45.67	—	100.00	Philipp, Ann. d. Chem. *184*, 132.
	,,	16.81	15.27	15.21	1.08	6.42	45.21	—	100.00	
		Si_{12}	Al_{12}	Ag_{16}	Na_2	S_4	O_{59}	$(H_2O)_4$		
3.	Theory.	9.39	9.06	48.28	1.29	3.58	26.39	2.01	100.00	
	Found.	9.78	9.40	48.82	1.07	3.96	26.07	1.90	100.00	J. Szilasi, Ann. d. Chem. *251*, 97-114.
	,,	8.63	9.42	48.79	1.03	4.03	26.29	1.81	100.00	
		Si_{12}	Al_{12}	Pb_3	Na_2	S_4	O_{59}	$(H_2O)_8$		
4.	Theory.	9.41	9.08	46.16	1.29	3.59	26.44	4.03	100.00	
	Found.	9.58	8.21	46.02	0.93	4.06	27.27	3.93	100.00	J. Szilasi, Ann. d. Chem. *251*, 97-114.
	,,	9.51	8.16	46.23	1.06	3.94	27.11	3.99	100.00	
		Si_{12}	Al_{12}	Zn_8	Na_2	S_4	O_{59}	$(H_2O)_{16}$		
5.	Theory.	12.99	12.53	20.11	1.77	4.95	36.51	11.14	100.00	
	Found.	14.14	11.80	19.78	—	5.86	37.52	10.90	100.00	J. Szilasi, Ann. d. Chem. *251*. 97-114.
	,,	14.17	11.86	19.98	0.72	5.66	36.51	11.10	100.00	
		Si_{12}	Al_{12}	Ag_{12}	Na_1	S_5	O_{56}	K		
6.	Theory.	10.69	10.31	44.67	0.73	5.09	28.51	—	100.00	
	Found.	10.76	9.90	43.69	0.81	4.89	29.60	0.35	100.00	J. Philipp. Ber. d. D. chem. Ges. *10*, 1227.
	,,	—	10.54	44.08	0.73	—	—	0.50	100.00	
		Si_{12}	Al_{12}	Ag_{15}	Na_1	S_6	O_{57}			
7.	Theory.	9.96	9.60	47.99	0.68	4.73	27.04	—	100.00	K. Heumann, Ann. d. Chem. *199*, 271.
	Found.	10.09	9.00	48.08	1.15	4.68	27.00	—	100.00	
	,,	10.09	9.11	47.89	1.17	4.82	26.92	—	100.00	
	,,	—	9.21	47.96	0.89	—	—	—	—	
	,,	10.24	9.23	48.66	—	4.81	—	—	—	K. Heumann, Ann. d. Chem. *203*, 174.
		Si_{12}	Al_{12}	Na_{12}	S_5	O_{64}				
8.	Theory.	16.86	16.27	13.85	9.64	43.33	—	—	100.00	
	Found.	16.80	16.32	13.94	9.70	43.24	—	—	100.00	G. Guckelberger, Dingl. Journ. *247*, 343, 1883.
	,,	16.84	16.30	13.98	9.80	43.08	—	—	100.00	

	Si_{12}	Al_{12}	Na_{16}	S_4	O_{52}	$(H_2O)_2$	Total	
9. Theory.	16.60	16.01	18.18	6.32	41.11	1.78	100.00	J. Szilasi, Ann. d. Chem. *251*, 97-114.
Found.	16.70	15.97	18.48	7.14	39.52	2.19	100.00	
,,	16.76	15.82	18.23	7.20	39.78	2.21	100.00	
,,	16.73	15.94	18.55	7.22	—	—	—	
,,	17.14	—	18.24	6.92	—	1.18	—	
,,	17.21	15.87	18.12	7.02	40.55	1.23	100.00	
,,	16.75	16.15	18.08	6.75	41.05	1.22	100.00	
,,	16.73	—	18.12	6.95	—	1.16	—	
,,	16.39	15.08	18.24	6.60	42.16	1.53	100.00	
,,	16.45	15.44	18.40	6.80	41.40	1.51	100.00	

	Si_{12}	Al_{12}	Na_{14}	K	S_5	O_{50}		
10. Theory.	17.30	16.68	16.59	—	8.24	41.19	100.00	
Found.	17.32	15.94	16.64	0.75	7.91	41.44	100.00	Philipp, Ann. d. Chem. *184*,132, 1876.
,,	17.51	15.84	17.08 (Na + K)		7.91	40.66	100.00	
,,	18.00	16.11	17.05	—	8.04	40.80	100.00	Hoffmann's Analyses, according to K. Heumann, Ann. d. Chem. *203*, 174. 1880.
,,	18.24	16.33	—	—	8.36	40.68	—	
,,	18.06	15.78	17.30	—	8.18	40.68	100.00	
,,	18.11	16.01	17.16	—	8.05	40.67	100.00	
,,	18.33	16.25	17.14	—	8.42	39.86	100.00	
,,	18.20	16.10	17.30	—	8.40	40.00	100.00	
,,	17.69	16.13	17.07	—	8.02	41.09	100.00	According to K. Heumann, Ann. d. Chem. *203*, 174, 1880.
,,	17.88	16.47	16.61	—	7.67	41.37	100.00	
,,	17.77	16.10	17.06	—	8.02	41.05	100.00	K. Heumann, Ann. d. Chem. *199*, 263.

	Si_{12}	Al_{12}	Na_{12}	S_4	O_{48}			
11. Theory.	18.34	17.69	15.07	6.98	41.92	—	100.00	
Found.	18.47	16.88	15.43	6.17	43.05	—	100.00	Rickmann, Dingl. Journl. *232*, 164.

	Si_{12}	Al_{12}	Na_{14}	S_4	O_{48}			
12. Theory.	17.89	17.25	17.14	6.83	40.89	—	100.00	
Found.	18.00	17.32	16.20	6.62	41.86	—	100.00	G. Guckelberger, Dingl. Journ. *247*, 343, 1883.
,,	18.28	17.15	16.40	6.78	41.39	—	100.00	
,,	18.30	17.38	16.10	6.59	41.63	—	100.00	
,,	17.98	17.30	16.52	6.88	41.32	—	100.00	
,,	18.08	17.35	16.46	6.69	41.42	—	100.00	
,,	17.89	17.43	16.38	6.89	41.41	—	100.00	
,,	18.41	17.00	16.40	6.81	41.38	—	100.00	G. Guckelberger Dingl. Journ. *247*, 386, 1883.
,,	18.21	17.63	16.80	7.01	40.35	—	100.00	
,,	18.08	17.32	17.01	6.89	40.70	—	100.00	
,,	18.00	17.68	16.92	7.05	40.35	—	100.00	
,,	18.90	17.82	16.21	6.40	40.67	—	100.00	
,,	18.34	17.60	16.78	6.79	40.49	—	100.00	
,,	18.61	17.12	16.38	6.75	41.14	—	100.00	
,,	17.86	17.56	16.60	6.79	41.19	—	100.00	G. Guckelberger, Dingl. Journ. *247*, 383, 1883.
,,	18.09	17.28	17.00	6.90	40.73	—	100.00	
,,	17.29	16.91	16.48	6.60	41.72	—	100.00	

	Si_{12}	Al_{12}	Na_{16}	S_4	O_{48}			
13. Theory.	17.46	16.84	19.13	6.65	39.92	—	100.00	
Found.	17.35	16.95	18.98	6.70	40 02	—	100.00	G. Guckelberger, Dingl. Journ. *247*, 343, 1883.
,,	17.52	16.84	18.88	6.60	40.16	—	100.00	
,,	17.65	16.50	18.98	6.72	40.15	—	100.00	
,,	17.67	16.40	19.05	6.80	40.08	—	100.00	G. Guckelberger, Dingl Journ. *247*, 383, 1883.
,,	17.83	16.41	18.97	6.62	40.17	—	100.00	
,,	18.01	16.24	19.20	6.78	39.77	—	100.00	
,,	18.02	17.00	18.92	6.82	39.24	—	100.00	G. Guckelberger Dingl. Journ. *247*, 386, 1883.

	Si_{12}	Al_{12}	Na_{12}	Ag_4	S_4	O_{48}	Total	
14. Theory.	14.84	14.31	12.19	19.08	5.65	33.93	100.00	
Found.	15.00	14.22	12.50	19.00	5.29	33.99	100.00	G. Guckelberger, Dingl. Journ. *247*, 343, 1883.
	Si_{12}	Al_{12}	Na_8	Ag_{10}	S_4	O_{43}		
15. Theory.	12.12	11.68	4.98	38.93	4.61	27.68	100.00	
Found.	12.02	11.82	4.58	39.20	4.40	27.98	100.00	G. Guckelberger, Dingl. Journ. *247*, 347, 1883.
	Si_{12}	Al_{12}	$Na_{13\cdot5}$	$K_{0\cdot5}$	S_4	O_{46}		
16. Theory.	18.12	17.48	16.75	1.05	6.90	39.70	100.00	
Found.	18.29	16.50	17.85	1.33	6.20	39.93	100.00	H. Ritter, Inaug.-Diss. Göttingen, 1860.
	Si_{12}	Al_{12}	Na_{18}	S_4	O_{43}			
17. Theory.	17.05	16.45	21.02	6.50	38.98	—	100.00	
Found.	17.00	16.60	21.50	6.50	38.40	—	100.00	Rickmann, Ann. d. Chem. *194*, 1-22.
„	16.74	15.95	20.59	6.22	40.50	—	100.00	} Rickmann, Dingl. Journ. *232*, 164.
„	16.59	16.14	20.92	5.72	40.63	—	100.00	
„	16.53	16.27	21.02	5.51	40.67	—	100.00	Rickmann, Dingl. Journ. *232*, 170.
	Si_{12}	Al_{12}	Na_{16}	S_4	O_{46}			
18. Theory.	17.75	17.12	19.45	6.77	38.91	—	100.00	
Found.	18.20	16.60	19.00	6.10	40.10	—	100.00	R. Hoffmann, Ann. d. Chem. *194*. 1-22, 1878.
	Si_{16}	Al_{12}	Na_{14}	S_9	O_{64}			
19. Theory.	18.62	13.47	13.38	11.97	42.56	—	100.00	
Found.	18.80	13.00	13.70	11.80	42.70	—	100.00	C. Grünzweig per R. Hoffmann, Ann. d. Chem. *194*, 18.
	Si_{16}	Al_{12}	Na_{16}	K	S_9	O_{65}		
20. Theory.	18.15	13.13	14.91	—	11.67	42.14	100.00	
Found.	17.29	12.55	14.66 (Na + K)		11.38	44.12	100.00	Philipp, Ann. d. Chem. *184*, 132, 1876.
„	17.57	12.54	14.51	0.80	11.38	43.20	100.00	
	Si_{12}	Al_6	Na_6	S_6	O_{38}			
21. Theory.	23.40	11.28	9.61	13.37	42.34	—	100.00	
Found.	23.12	11.71	8.97	13.22	42.98	—	100.00	G. Scheffer, Ber. d. D. Chem. Ges. 1451, 1873.
	Si_{10}	Al_6	Na_6	S_6	O_{34}			
22. Theory.	20.77	12.02	10.24	14.24	42.73	—	100.00	
Found.	21.63	12.33	9.93	13.96	42.15	—	100.00	G. Scheffer, Ber. d. D. Chem. Ges. 1451, 1873.
	Si_{18}	Al_{12}	Na_{20}	S_{10}	O_{62}			
23. Theory.	17.61	12.74	18.08	12.58	38.99	—	100.00	
Found.	17.70	13.80	17.70	12.20	38.60	—	100.00	R. Hoffmann, Ann. d. Chem. *194*, 14. 1878.
	Si_{18}	Al_{12}	Na_{14}	Si_{12}	O_{59}			
24. Theory.	20.34	13.08	12.99	15.50	38.09	—	100.00	
Found.	20.20	13.50	12.90	15.50	37.09	—	100.00	R. Hoffmann, Ann. d. Chem. *194*, 17, 1878.
	Si_{18}	Al_{12}	Na_{18}	S_{12}	O_{61}			
25. Theory.	19.37	12.45	15.91	14.76	37.51	—	100.00	
Found.	19.20	12.60	16.50	14.20	37.50	—	100.00	} G. Guckelberger, Dingl. Journ. *247*, 343, 1883.
„	19.00	12.70	16.80	14.00	37.50	—	100.00	
„	19.00	13.00	16.50	13.80	37.70	—	100.00	
„	19.30	12.50	16.80	13.90	37.50	—	100.00	
„	19.30	12.80	16.10	14.00	37.80	—	100.00	
„	19.00	13.00	15.90	14.00	38.10	—	100.00	
	Si_{18}	Al_{12}	Na_{20}	S_{12}	O_{63}			
26. Theory.	18.92	12.17	17.27	14.42	37.22	—	100.00	
Found.	19.00	12.70	17.40	13.60	37.30	—	100.00	R. Hoffmann, Dingl. Journ. *247*, 1883; Ann. d. Chem. *194*, 14.
	Si_{16}	Al_{12}	Na_{12}	S_{12}	O_{56}			
27. Theory.	19.00	13.74	13.66	16.28	37.32	—	100.00	
Found.	18.80	13.80	14.10	16.30	37.00	—	100.00	R. Hoffmann, Ann. d. Chem. *194*, 17.

	Si_{12}	Al_6	Na_8	S_6	O_{36}	Total	
28. Theory.	23.17	11.18	12.69	13.24	39.72	100.00	
Found.	23.04	10.77	11.90	14.02	40.27	100.00	G. Scheffer, Ber. d. D. chem. Ges. 1451, 18
,,	23.63	11.09	12.00	13.46	39.82	100.00	
	Si_{16}	Al_{12}	Na_{18}	S_6	O_{60}		
29. Theory.	21.47	13.79	15.68	8.18	40.88	100.00	
Found.	21.53	13.42	15.38	9.25	40.42	100.00	E. Büchner, Ber. d. D. chem. Ges. *7*, 989, 18
	Si_{13}	Al_{12}	Na_{18}	S_5	O_{62}		
30. Theory.	21.05	13.55	17.29	6.68	41.43	100.00	
Found.	20.75	13.53	17.01	6.78	41.93	100.00	
,,	21.00	13.08	16.98	6.79	42.15	100.00	
,,	20.89	13.28	17.28	6.80	41.75	100.00	G. Guckelberger, Dingl. Journ. *247*, 343, 18
,,	20.51	13.50	18.00	6.90	41.09	100.00	
,,	21.00	13.12	17.80	7.02	41.06	100.00	
,,	20.69	13.30	17.20	6.90	41.91	100.00	

Portland Cements

Formulæ of a Series from Analyses of Portland Cements

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	CO_2	SO_3	H_2O	Total	
1. Theory.	25.34	5.37	8.39	50.89	1.39	0.82	0.54	4.61	1.39	1.26	100.00	
Found.	25.29	5.41	8.64	50.40	1.24	0.50	0.73	4.61	1.10	1.30	99.92	Feichtinger, Dingl. Journ., 40- 108-118, 18
2. Theory.	24.09	6.83	5.35	63.73	—	—	—	—	—	—	100.00	
Found.	24.30	6.90	4.80	64.10	—	—	—	—	—	—	100.10	A. W. Hoffmann, Amtl. Ber Wien. Ausst. *3*, I, 583, 18
3. Theory.	23.65	6.70	5.26	64.39	—	—	—	—	—	—	100.00	
Found.	23.30	6.50	4.70	65.40	—	—	—	—	—	—	99.90	
4. Theory.	22.78	6.45	5.06	63.78	0.67	—	—	—	1.26	—	100.00	
Found.	22.48	6.52	4.46	62.93	1.48	—	—	—	1.39	—	99.26	K. Pietrusky, J. B. T. *48*, 1, 4
,,	21.94	6.02	4.38	64.63	1.25	—	—	—	1.12	—	99.34	Chem. Ind. 1
,,	23.44	6.35	3.99	63.21	1.15	—	—	—	1.22	—	99.36	
5. Theory.	22.50	6.38	5.00	63.00	1.88	—	—	—	1.24	—	100.00	
Found.	22.00	6.50	3.20	62.10	2.10	—	—	—	1.10	—	97.00	J. B. T. *43*, 765.
,,	22.42	6.28	3.62	62.82	2.09	—	—	—	1.29	—	98.52	
,,	22.10	6.25	3.70	62.50	1.75	—	—	—	1.20	—	97.50	
,,	22.07	6.59	3.41	62.00	1.04	—	—	—	1.53	—	96.64	
6. Theory.	22.59	6.36	4.98	63.26	1.56	—	—	—	1.25	—	100.00	
Found.	22.48	6.52	4.46	62.93	1.48	—	—	—	1.30	—	99.17	Tonind.-Ztg., 1826, 1901.
,,	23.44	6.35	3.99	63.21	1.15	—	—	—	1.22	—	99.36	
Theory.	22.30	7.06	3.69	62.02	2.46	—	—	—	2.46	—	100.00	
Found.	21.86	7.17	3.73	61.14	2.34	—	—	—	1.94	—	98.18	Tonind.-Ztg., 1826, 1901.
8. Theory.	22.22	7.03	3.67	65.23	0.61	—	—	—	1.23	—	100.00	
Found.	22.10	6.40	3.04	65.44	0.81	—	—	—	1.61	—	99.40	Tonind.-Ztg., 2015, 1901.
9. Theory.	21.83	6.13	4.82	64.50	1.51	—	—	—	1.21	—	100.00	
Found.	21.94	6.02	4.38	64.62	1.25	—	—	—	1.12	—	99.33	
10. Theory.	21.55	7.58	2.38	64.93	1.19	—	—	—	2.37	—	100.00	
Found.	21.26	7.64	2.86	63.74	1.10	—	—	—	2.18	0.60	99.38	Tonind.-Ztg., 2015, 1901.
11. Theory.	23.71	12.10	—	64.19	—	—	—	—	—	—	100.00	
Found.	23.80	11.40	—	64.80	—	—	—	—	—	—	100.00	A. W. Hoffmann, Amtl. Ber Wien. Ausst. *3*, I, 583, 18
12. Theory.	21.17	8.04	4.20	61.82	3.50			—	—	1.27	100.00	
Found.	20.72	7.57	4.48	60.52	3.02	1.02		0.52	0.37	1.22	99.44	Fischer, H. d. ch. T. 828.
13. Theory.	20.64	7.89	4.13	62.59	2.06	1.62	1.07	—	—	—	100.00	
Found.	20.33	8.67	3.80	62.33	2.48	1.20	0.85	—	—	—	99.66	J. B. T. *43*, 732.
,,	20.33	7.19	3.65	63.65	2.62	1.04	0.80	—	—	—	99.28	
14. Theory.	24.15	—	10.73	65.12	—	—	—	—	—	—	100.00	
Found.	23.80	—	11.40	64.80	—	—	—	—	—	—	100.00	A. W. Hoffmann, Amtl. Ber Wien. Ausst. *3*, I, 583, 18

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	CO_2	SO_3	H_2O	Total	
15. Theory.	23.65	5.02	2.63	65.87	1.09			—	1.74	—	100.00	
Found.	23.40	5.18	2.79	65.80	1.13	0.48		—	1.42	—	100.20	Loebell, J. B. T. *48*, 1.
„	32.68	5.03	2.82	65.47	1.08	0.53		—	1.36	—	99.97	466.
16. Theory.	32.52	7.37	5.79	44.56	1.45	0.85	0.57	4.78	1.46	0.66	100.00	
Found.	32.60	7.17	6.23	44.96	1.52	0.45	0.64	4.52	1.20	0.72	100.00	Fehling, H. d. Chem. 482,
17. Theory.	34.15	7.73	6.06	46.76	0.76	—	—	1.66	1.51	1.37	100.00	1875.
Found.	34.07	7.49	5.58	46.07	0.90	—	—	1.38	1.96	1.47	98.92	Fehling, H. d. Chem. 482,
18. Theory.	32.63	7.34	5.76	45.37	1.44	0.85	0.56	3.96	1.44	0.65	100.00	1875.
Found.	32.60	7.17	6.23	44.96	1.52	0.45	0.64	4.52	1.20	0.72	100.01	Feichtinger, Dingl. Jour.
19. Theory.	34.08	7.67	6.02	46.33	0.75	0.88	0.58	0.82	1.50	1.35	100.00	40–61, 108–118, 1859.
Found.	34.07	7.49	5.58	46.07	0.90	0.27	0.56	1.38	1.96	1.47	99.75	Feichtinger, Dingl. Jour.
20. Theory.	29.33	4.95	7.72	48.01	1.94	0.05	0.50	5.69	0.65	1.16	100.00	40–61, 108–118, 1859.
Found.	28.56	4.75	8.14	47.53	2.04	0.48	0.68	5.58	0.40	1.20	99.36	Feichtinger, Dingl. Jour.
21. Theory.	28.89	4.92	7.71	48.47	1.93	0.76	0.50	5.66	—	1.16	100.00	40–61, 108–118, 1859.
Found.	28.56	4.75	8.14	47.53	2.04	0.48	0.60	5.58	—	1.20	98.88	Fehling, H. d. Chem. 482,
22. Theory.	25.39	7.19	2.26	56.87	2.82	1.33	0.87	1.00MnO	2.27	—	100.00	1875.
Found.	24.26	6.97	2.88	56.90	2.15	0.90	0.54	1.60MnO	1.28	—	97.48	J. B. T. *44*, 749.
24. Theory.	23.35	6.57	2.06	64.93	1.03	—	—	—	2.06	—	100.00	
Found.	22.96	6.78	2.54	63.95	0.98	—	—	—	1.96	—	99.17	Tonind.-Ztg. 2015, 1901.
25. Theory.	23.19	5.87	3.06	63.03	1.02	0.60	1.19	—	2.04	—	100.00	
Found.	23.40	6.07	2.51	63.87	0.97	0.80	1.22	—	1.45	—	100.29	v. Teichek, Chem. Ind.
26. Theory.	23.21	5.92	3.09	65.72	1.03	—	—	—	1.30	—	100.00	*24*, 445, 1901.
Found.	22.71	6.42	2.81	63.14	1.04	1.64 $CaSO_4$		0.80$CaCO_3$	—	—	93.56	Tonind.-Ztg. 409, 1879.
27. Theory.	22.94	5.81	3.03	65.18	1.02	—	—	—	2.02	—	100.00	
Found.	22.33	5.53	3.28	64.40	1.20	—	—	—	2.41	—	99.15	Tonind.-Ztg. 2015, 1901.
28. Theory.	10.39	7.37	2.31	71.96	3.47			1.91	—	2.59	100.00	
Found.	10.38	6.66	1.99	72.10	3.27	0.85		1.64	0.43	2.56	99.88	Fischer, H. d. ch. T. 828.
29. Theory.	25.29	8.35	9.36	52.43	—	—	0.72	2.06	0.94	0.85	100.00	
Found.	25.21	8.26	8.35	52.46	—	—	0.78	2.25	1.30	0.68	99.29	Fehling, H. d. Ch. 482,
30. Theory.	25.13	8.25	9.24	52.42	0.46	—	0.71	2.03	0.92	0.83	100.00	1875.
Found.	25.21	8.26	8.35	52.46	0.50	0.30	0.78	2.25	1.30	0.68	100.09	Feichtinger. Dingl. Jour.
31. Theory.	17.25	8.18	2.57	63.71	3.85			2.12	—	2.32	100.00	40–61, 108–118, 1859.
Found.	16.75	7.97	2.71	61.92	4.03	1.25		2.42	0.42	2.24	94.64	Fischer, H. d. ch. T. 828.
32. Theory.	17.71	8.37	2.62	66.12	3.28			0.72	—	1.18	100.00	
Found.	17.04	8.09	3.25	65.05	3.04	0.92		0.83	0.30	1.06	99.58	Fischer, H. d. ch. T. 828.
33. Theory.	15.00	7.03	2.20	66.44	4.41			2.42	—	2.50	100.00	
Found.	14. [illegible]	7.52	2.15	65.42	3.89	0.86		2.19	0.52	2.32	99.63	Fischer, H. d. ch. T. 828.
34. Theory.	21.78	13.89	—	45.06	3.18	—	—	2.00	1.83	12.26	100.00	
Found.	21.02	13.02	—	43.57	3.09	—	—	1.76	2.29	11.87	96.62	J. B. T. *44*, 745.
35. Theory.	20.59	13.04	—	42.64	2.77	1.01	0.66	1.40	2.55	13.82	98.48	
Found.	20.22	14.52	—	41.87	3.02	0 77	0.71	1.86	3.02	13.77	99.76	Zulkowski.
36. Theory.	24.59	15.68	0.91MnO	48.77	3.08	2.41	1.59	0.92 FeO	2.05	—	100.00	Zulowski,
Found.	24.64	15.27	0.82MnO	49.70	3.29	1.67	1.37	1.12 FeO	1.72	—	99.60	J. B. T. *44*, 745.
37. Theory.	21.04	13.32	0.78 FeO	43.57	2.83	1.02	1.35	0.96	2.61	11.75	100.00	0.77 MnO.
Found.	21.02	13.02	0.85 FeO	43.57	3.09	0.31	0.84	1.76	2.29	11.87	99.28	0.66 MnO Zulkowski.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	CO_2	SO_3	H_2O	Total	
38. Theory.	24.73	15.65	0.92 FeO	49.77	3.32	1.80	1.59	0.28	1.03	0.91 MnO	100.00	
Found.	24.64	15.27	1.12 FeO	49.70	3.29	1.67	1.37	0.54	1.72	0.82 MnO	100.14	Zulkowski
39. Theory.	23.71	7.78	5.23	54.37	0.87	1.02	2.03	3.14	0.87	0.98	100.00	
Found.	22.23	7.75	5.30	54.10	0.75	1.10	1.66	2.15	1.00	1.00	97.04	Feichtinger, Dingl. Journ.
"	23.72	7.36	5.50	54.40	0.86	0.86	1.78	2.80	1.12	0.96	99.36	40·61, 108–118, 1859.
40. Theory.	23.64	8.93	3.51	61.29	0.87	—	—	—	1.76	—	100.00	
Found.	22.47	7.81	3.42	61.13	1.06	—	—	—	2.03	—	97.92	J. B. T. *35*, 852.
"	23.57	8.89	3.51	60.10	0.95	—	—	—	0.90	—	97.92	
"	22.96	9.14	3.23	61.19	1.03	—	—	—	1.45	—	99.00	
"	23.36	8.12	3.21	60.57	1.19	—	—	—	1.81	—	98.26	
41. Theory.	28.72	3.05	1.59	65.85	0.79	—	—	—	—	—	100.00	
Found.	28.54	3.43	1.13	66.62	0.30	—	—	—	—	—	100.02	
"	29.08	3.40	1.24	66.07	0.20	—	—	—	—	—	99.99	Tonind.-Ztg. 981, 1902.
42. Theory.	27.39	2.92	1.52	68.17	—	—	—	—	—	—	100.00	
Found.	27.06	3.19	1.29	68.06	0.35	—	—	—	—	—	99.95	
43. Theory.	26.49	3.75	—	69.03	0.73	—	—	—	—	—	100.00	
Found.	26.30	3.50	0.77	68.84	0.54	—	—	—	—	—	99.95	
44. Theory.	23.96	3.38	—	72.66	—	—	—	—	—	—	100.00	
Found.	23.75	3.11	0.85	72.01	0.30	—	—	—	—	—	100.02	

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